Chemical Kinetic Data Base for Combustion Chemistry. Part I. Methane and Related Compounds

W. Tsang and R. F. Hampson

Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899

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This document contains evaluated data on the kinetics and thermodynamic properties of species that are of importance in methane pyrolysis and combustion. Specifically, the substances considered include H, H_2, O, O_2, OH, HO_2, H_2O_2, H_2O, CH_4, C_2H_6, HCHO, CO_2, CO, HCO, CH_3, C_2H_5, C_2H_4, C_2H_3, C_2H_2, C_2H, CH_3CO, CH_3O_2, CH_3O, singlet CH_2, and triplet CH_2. All possible reactions are considered. In arriving at recommended values, first preference is given to experimental measurements. Where data do not exist, a best possible estimate is given. In making extrapolations, extensive use is made of RRKM calculations for the pressure dependence of unimolecular processes and the BEBO method for hydrogen transfer reactions. In the total absence of data, recourse is made to the principle of detailed balancing, thermokinetic estimates, or comparisons with analogous reactions. The temperature range covered is 300–2500 K and the density range 1×10^{16}–1×10^{21} molecules/cm^3. This data base forms a subset of the chemical kinetic data base for all combustion chemistry processes. Additions and revisions will be issued periodically.

Key words: chemical kinetics; combustion; data evaluation; methane; oxidation; pyrolysis; rate constants.

Contents

1. Preface

1.1. Scope

This collection of chemical kinetic rate data and related information is intended for the use of those interested in developing a detailed understanding of gas phase combustion processes involving organic fuels. This includes those who use such information in order to simulate complex phenomena and others involved in generating data through laboratory or theoretical efforts. At the present time, this data base is limited to those reactions pertinent to the combustion of methane. It is further restricted to reactions involving one and two carbon atom systems. Thus the chemical phenomena to which this data base may be applied are the initial stages of the combustion of C_1 and C_2 hydrocarbons. The data base also covers the pyrolytic behavior of such systems. Due to the nature of the information base, chemical processes under ambient conditions are also covered. Indeed, the major thrust of this effort involves the extrapolation of the much more plentiful lower temperature results to combustion conditions. As a result, the data base is pertinent to the full range of oxidative phenomena. It is our intention to continually enlarge and upgrade the data base so that an increasingly wider range of chemical phenomena can be covered.

This initial effort involving the simplest of organic compounds is dictated by the following considerations. First, the reactions that are covered form a subset of processes of importance to any hydrocarbon combustion system. Second, the volume of work in the area is more extensive than that of more complex organics. Finally, as the beginning of the homologous series, the rate constants of these processes form the basis of predictions on more complex organics.

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1.2. Organization

The information in this manuscript is organized into several sections. The first part contains a tabulation of all the recommended rate expressions and their estimated uncertainties. Also included are the page numbers where the more complete discussion of the reaction can be found. The second section contains background information on the individual reactions. The format is similar to previous NBS reports[1] on rate data for stratospheric modeling. The selection of reactions to be covered was dictated by the species that can be expected to be present in any methane combustion system. Following our experience with the stratospheric chemistry situation, a reaction grid containing 25 species was constructed (see Fig. 1). We then considered all possibilities for reactions of each species with each other and for unimolecular decomposition. In a number of cases, it is fairly obvious that the processes need not be considered; for example $H + H_2 \rightarrow H_2 + H$ or $CH_4 + C_2H_6$, where the only possible process, $CH_4 + C_2H_6 \rightarrow CH_4 + 2CH_3$, is subsumed under the unimolecular decomposition category. In all other cases rate constants are given for the temperature range 300–2500 K and density range 1×10^{16}–1×10^{21} molecules cm^{-3}. These should encompass every possible oxidation and pyrolysis regime.

Thermodynamic data are important inputs for the estimation and evaluation of kinetic information. Tables of thermodynamic properties over the temperature range 300–1500 K for the 25 species are given in Sec. 4. In addition, for unimolecular reactions, transport properties are needed for the estimation of collision efficiencies. A short table of the necessary information is included in Sec. 5.

1.3. Guide to Summary Table

This contains a summary of our evaluated values. The three columns contain statements on the reaction process, the appropriate rate expression, and the estimated uncertainty. In the case of unimolecular processes we give the rate constant ratios for 1 atm N_2 and, as appropriate, the infinite or zero pressure rate expression.

1.4. Guide to Chemical Kinetic Data Tables

Each of the reactants is assigned a number from 2 to 26 (see Fig. 1). Number 1 is reserved for unimolecular processes. The array of two numbers defines a particular reaction. The ordering of reactions begins with a reactant with a particular sequence number and then considers all reactants with lower sequence numbers. The absence of a reaction implies that the rate constant is too small to be of interest for any conceivable situation.

The sequence number can be found at the top of the data sheet. It is then followed by a statement of the chemical

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
		M	$H2$	O_2	H	O	OH	HO_2	H_2O_2	H_2O	CH_4	C_2H_6	HCHO	CO_2	CO	HCO	CH_3	C_2H_5	C_2H_4	C_2H_3	C_2H_2	C_2H	CH_3CO	CH_3O_2	CH_3O	$^1CH_2$	$^3CH_2$
1	M																										
2	H_2	x																									
3	O_2	x	x																								
4	H			x	x																						
5	O		x		x	x																					
6	OH	x	x	x	x	x	x																				
7	HO_2	x	x		x	x	x	x																			
8	H_2O_2	x		x	x	x	x																				
9	H_2O	x			x	x																					
10	CH_4	x		x	x	x	x	x																			
11	C_2H_6	x		x	x	x	x	x																			
12	HCHO	x		x	x	x	x	x																			
13	CO_2				x	x																					
14	CO			x	x	x	x	x																			
15	HCO	x	x	x	x	x	x	x	x	x	x	x				x											
16	CH_3		x	x	x	x	x	x	x	x		x	x		x	x	x										
17	C_2H_5	x	x	x	x	x	x	x	x	x	x		x		x	x	x	x									
18	C_2H_4	x	x	x	x	x	x	x							x		x	x	x								
19	C_2H_3	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x							
20	C_2H_2	x	x	x	x	x	x	x							x		x	x	x		x						
21	C_2H		x	x	x	x	x	x			x	x			x	x	x	x	x	x	x	x					
22	CH_3CO	x	x	x	x	x	x	x	x		x	x	x			x	x	x		x		x	x				
23	CH_3O_2	x	x		x	x	x	x	x		x	x	x			x	x	x		x		x	x	x			
24	CH_3O	x		x	x	x	x	x			x	x	x		x	x	x	x	x	x	x	x	x	x	x		
25	$^1CH_2$	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
26	$^3CH_2$	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x

FIG. 1. Reaction grid (x: evaluations).

reaction. All the reactions listed are elementary reactions. The reaction statement will, where applicable, be followed by the equilibrium constant of the reaction. This is expressed in the form

$$\log K_p = A + B/T + C/T^2 + D/T^3 .$$

Accuracy across the appropriate temperature ranges is in the range of 1%–2%. Thus all the other thermodynamic functions can be derived to reasonable accuracy using standard relations.

The next section on the data sheet contains a synopsis of previous work. It begins in the first column with a listing of the author(s) and the year of publication. The ordering is from the latest to the earliest work. A specific statement is made if the reference is a review. In many cases, we have used earlier reviews as a starting point for our analysis. Readers must therefore turn to the references in these reviews if they are interested in the earlier work. Columns 2 and 3 contain information on the experimental conditions used in the investigations. Column 4 gives the rate expressions that have been obtained. Most of the processes are bimolecular. In the cases where they are unimolecular the specific units s^{-1} are given, while for termolecular processes the units of cm^6 molecule^{-2} s^{-1} are used. The final column contains information on uncertainty limits. Most of these are the estimates of the investigators.

The next section contains our recommendations and a brief discussion of our rationale. It should be emphasized that at the present time there is no standard method for carrying out data evaluation in chemical kinetics. The following represents our methodology. First preference is given to experimental determinations where the mechanism is clear cut. Frequently, this is from direct determinations of the rate of change of reactants or intermediates in real time. It has also been our experience that in a complex situation where careful and complete final (stable) product analyses are carried out very satisfactory results can be achieved. In the absence of chemical kinetic data, thermodynamic considerations in the form of detailed balance are used. In other cases, rate constants are assigned on the basis of analogy and/or thermokinetic considerations. The uncertainty statement represents an estimate by the evaluator of the absolute accuracy of the recommended rate expression. It is strictly a subjective number based on the intercomparison of the data sets, considerations of related reaction mechanisms, and the constraints imposed by thermodynamics and theory. Quantitatively, it means that in the evaluator's judgment the true value will be within the indicated limits to a high degree of confidence.

Rate theory is used in these evaluations only as a method for extrapolation. For metathetical reactions involving H atoms, the Bond Energy Bond Order method (BEBO) of Johnston[2] is used to derive the curvature of the Arrhenius plot. Details of the procedure used can be found in a paper by Brown.[3] We have found, as have others, that on an absolute basis BEBO results are unreliable. Instead, we have used the BEBO methodology to derive the transition state structure. The activation energy is adjusted so as to reproduce the experimental data at specific temperature(s). The general result is a temperature dependence of the pre-exponential factor in the T^2 to the T^4 range. This is in fair accord with experimental evidence. The lack of sufficient data over a large temperature range prevents a systematic check of this procedure and we have noted some tendencies to overestimate this temperature dependence by our procedure.

Unimolecular reactions and associated processes are rendered more complex than metathesis reactions by their dependence not only on reaction temperature but also pressure and the nature of the substances present. We have applied standard Rice–Ramsperger–Kassel–Marcus (RRKM) type calculations as a framework for projecting data over all relevant temperature and pressure ranges. The computational procedure has been checked by reproducing the results published in Robinson and Holbrook,[4] Hassler and Setser,[5] and Troe.[6] More details of the methodology used in fitting the data will be given in a subsequent paper.[7] We have not been able to derive a closed expression that encompasses all the possible reaction conditions. The results are given in the data sheets in the form of tables and some manipulation of the information is necessary. In the case of unimolecular decompositions or the reverse combination processes an expression is given for the rate constant at the high-pressure limit, or as appropriate, at the low-pressure limit, assuming collisional deactivation on every collision (strong collision assumption). The choice of either reference condition is dictated by the desire to minimize what are essentially the correction factors to the given rate expressions. The latter can be found in the tables in the appropriate data sheets.

One of the tables in the data sheets gives k/k^{∞} or k/k_0, where k is the strong collision rate constant, the collision partner is the reactant itself and k^{∞} and k_0 are the limiting infinite pressure and zero pressure values, respectively. Thus in the cases where the high-pressure rate expression k^{∞} is given, rate constants on a strong collision basis can be calculated by multiplying this limiting value at the desired temperature and pressure with the appropriate value of k/k^{∞} as obtained from the table. Since under high-temperature conditions the strong collision assumption is not satisfactory, a second table in the data sheets gives β_c, the collision efficiency (on a per collision basis) as a function of step size down (energy removed per collision). The numbers in the table are derived from the equation given by Troe.[6] At the present time, there is some uncertainty with regard to the appropriate value to be used. We have thus cast the data in this form so that the reader may use his own step sizes. The values of β_c given here are for the reactant molecule as its own collision partner. For the more general case with any collision partner, it is necessary to use the approach of Troe[6] and derive a correction factor β_e which when multiplied by the β_c given above yields the total collisional efficiency $\beta_t = \beta_c * \beta_e$ which is the quantity needed to derive the rate constant from the information given in the two tables and the limiting rate expressions. Specifically, it involves the calculation of a number of ratios that account for the differences in the transport properties of the collision partners. The necessary quantities are given below and we also illustrate the situation for a methane and argon mixture at 2000 K:

(a) Ratio of reduced masses (R); for a methane–argon mixture this number is $11.43/8 = 1.429$, where 8 is the reduced mass for methane–methane collisions and 11.43 is the reduced mass for methane–argon collisions.

(b) Ratio of collision diameters (C); for a methane–argon mixture this value is $(3.758 + 3.542)/(3.758\times 2) = 0.971$. Note that the values for these parameters can be found in a table in Sec. 5.

(c) Ratio of collision integrals (W); where we use the approximation $w' = 1/\{0.679 + 5.85 \log[kT/\epsilon(\mathrm{am})]\}$ and $\epsilon(\mathrm{am})/k = \{[\epsilon(\mathrm{a})/k]\,[\epsilon(\mathrm{m})/k]\}^{0.5}$, where $\epsilon(\mathrm{a})$, $\epsilon(\mathrm{m})$, and $\epsilon(\mathrm{am})$ are the Lennard Jones well depths for argon, methane, and argon–methane. Since ϵ/k for methane is 148.6 K and 93.3 K for argon, then the ratio of the collision integrals is $0.759/0.791 = 0.96$ at 2000 K.

When these ratios are grouped together we obtain the factor

$$\beta_c = C^2 W/(R)^{0.5} .$$

When this is multiplied by the collision efficiency β_c on a per collision basis as determined from the table, for a given step size we obtain the total collisional efficiency $\beta_t = \beta_e * \beta_c$. Multiplication of the reaction pressure with β_t leads to an equivalent strong collision pressure. k/k^∞ can then be read directly from another table. Thus in the case of methane at 2000 K a step size down of 600 cm^{-1} will lead to a collision efficiency of 0.06. With argon as the collisional partner, the correction factor given above yields a value of 0.755. The total collision efficiency is 0.047. This means that in our methane–argon mixture, a reaction density of 1×10^{18} molecules cm^{-3} is equivalent to a strong collision reaction density of 4.7×10^{16} molecules cm^{-3} and at our hypothetical 2000 K temperature, Table A in our data sheet for methane decomposition (reaction 10,1) yields a k/k^∞ value of approximately 0.004. From the above, it is clear that the major weak collision effect arises from the choice of the step size down. The correction, taking into account collisional properties, is in most cases within the experimental uncertainty.

For those systems where the low-pressure rate expressions k_0 are given, the same procedure should be followed except that the final rate constant is $\beta_t \times k_0 \times (k/k_0)$. For chemical activation processes, the rate constants can be obtained in an analogous manner. In addition to the possible pressure dependence in the total rate, the ratio of decomposition to stabilization is also of importance. Thus as required we include an additional table giving this ratio as a function of temperature and pressure. Our treatment of such processes in this manner must be considered a rough approximation. In view of the lack of data and inherent uncertainties a more rigorous treatment is not justified at the present time.

As an additional aid to the user, the rate constant ratios which may be derived from the tables in those data sheets that are concerned with unimolecular processes are given as closed expressions for nitrogen and the reactant molecule as the weak colliders at pressures of 0.1, 1, and 10 atm. These are based on a step size down to 400–800 cm^{-1} for nitrogen and 1000–2000 cm^{-1} for the reactant molecule. They are based on our assessment of the existing data base. The expressions should be applicable from 800 K on up. The relations are definitely not applicable in the lower temperature regions where our analysis shows that for weak colliders the step size down is very small.

The last section of the data sheet contains the references used in this evaluation, the evaluator, and a date. Hopefully, all of the literature on this reaction previous to this date has been accessed. The authors would be very grateful to those readers who will bring to their attention publications that they may have missed or subsequent investigations which should be included in future publications.

1.5. Guide to Thermodynamic and Transport Tables

Section 4 contains tables of thermodynamic properties of the species considered in this evaluation. The temperature range covered is 300–1500 K. The properties tabulated include the entropy, heat capacity, enthalpy of formation, and the Gibbs energy of formation. In addition, we give in polynomial form a closed expression for the equilibrium constant of formation K_p. These fit the data to within 1% or 2%. Most of the values are abstracted from standard sources.[8] In certain cases, we have made our own calculations. The molecular properties used in deriving these numbers are in a footnote. In the case of the JANAF Tables, we have not used the latest addendum. For the compounds in question, this does not introduce any error. The transport properties are taken from Reid, Prausnitz, and Sherwood.[9] For the radical species that do not appear in the table, we have taken average values using the corresponding alkanes and alkenes as a base.

1.6. Acknowledgments

This work was supported by the Department of Energy, Division of Basic Energy Sciences and the Office of Standard Reference Data, National Bureau of Standards. We are particularly grateful to the late Dr. O. W. Adams for his constant encouragement and support during the course of this work. We are grateful to Dr. John T. Herron, Director, Chemical Kinetics Data Center and Dr. R. J. Cvetanovic for their careful reading of the manuscript. We are especially indebted to Mrs. Geraldine Zumwalt and Ms. Rhoda Levin for their attention to many details in the keyboarding, editing, and the preparation of the final copy of this large collection of detailed data sheets.

1.7. References to the Introduction

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2. Index of Reactions and Summary of Recommended Rate Expressions

No.	Reaction	Rate Constant $k/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\mathrm{s}^{-1}$	Uncertainty factor	Page
2,1	$H_2 + M \rightarrow H + H + M$	$7.6\mathrm{x}10^{-5}T^{-1.4}\exp(-52530/T)$ 600-2000 K (M=N_2)	3	1108
3,1	$O_2 + M \rightarrow O + O + M$	$3.0\mathrm{x}10^{-6}T^{-1}\exp(-59380/T)$ (M=Ar)	2	1108
3,2	$O_2 + H_2 \rightarrow H + HO_2$	$2.4\mathrm{x}10^{-10}\exp(-28500/T)$	5	1109
4,3	$H + O_2 \rightarrow OH + O$	$2.8\mathrm{x}10^{-7}T^{-0.9}\exp(-8750/T)$ 300-1250 K	2 to 1.3	1109
	$H + O_2 + M \rightarrow HO_2 + M$	$17.7\mathrm{x}10^{-30}T^{-1}\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{s}^{-1}$ (M=O_2,N_2)		
4,4	$H + H + M \rightarrow H_2 + M$	$1.5\mathrm{x}10^{-29}T^{-1.3}\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{s}^{-1}$ 77-2000 K (M=N_2)	2	1110
5,2	$O + H_2 \rightarrow OH + H$	$1.8\mathrm{x}10^{-20}T^{2.8}\exp(-2980/T)$	1.6 (400-1600K), 2 at 1600 K	1111
5,4	$O + H + M \rightarrow OH + M$	$1.3\mathrm{x}10^{-29}T^{-1}\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{s}^{-1}$	10	1111
5,5	$O + O + M \rightarrow O_2 + M$	$5.2\mathrm{x}10^{-35}\exp(900/T)$ $\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{s}^{-1}$ 200-4000 K (M=Ar)	1.3	1112
6,1	$OH + M \rightarrow O + H + M$	$4.0\mathrm{x}10^{-9}\exp(-50000/T)$	10	1112
6,2	$OH + H_2 \rightarrow H + H_2O$	$1.06\mathrm{x}10^{-17}T^{2}\exp(-1490/T)$ 240-2400 K	1.4 to 3	1113
6,3	$OH + O_2 \rightarrow O + HO_2$	$3.7\mathrm{x}10^{-11}\exp(-26500/T)$	3	1113
6,4	$OH + H \rightarrow O + H_2$ (a)	$8.1\mathrm{x}10^{-21}T^{2.8}\exp(-1950/T)$ 300-2500 K	2	1114
	$OH + H + M \rightarrow H_2O + M$ (b)	$6.1\mathrm{x}10^{-26}T^{-2}\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{s}^{-1}$ 300-3000 K (M=N_2)	2	
6,5	$OH + O \rightarrow H + O_2$	$7.5\mathrm{x}10^{-10}T^{-0.5}\exp(-30/T)$ 200-2500 K	1.4	1115
6,6	$OH + OH \rightarrow H_2O + O$	$3.5\mathrm{x}10^{-16}T^{1.4}\exp(200/T)$	2	1115
	$OH + OH + M \rightarrow H_2O_2 + M$	$1.6\mathrm{x}10^{-23}T^{-3}\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{s}^{-1}$ 500-2500 K <10 atm (M=N_2)	2	

Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
7,1	$HO_2 + M \rightarrow H + O_2 + M$	$2.0x10^{-5}T^{-1.18}exp(-24363/T)$ 200-2200 K ($M=N_2$)	3	1117
7,2	$HO_2 + H_2 \rightarrow H_2O_2 + H$	$5.0x10^{-11}exp(-13100/T)$	3	1117
7,4	$HO_2 + H \rightarrow 2OH$ (a)	$2.8x10^{-10}exp(-440/T)$	2	1118
	$\rightarrow H_2 + O_2$ (b)	$1.1x10^{-10}exp(-1070/T)$	2	
7,5	$HO_2 + O \rightarrow OH + O_2$	$2.9x10^{-11}exp(+200/T)$	1.2	1119
7,6	$HO_2 + OH \rightarrow H_2O + O_2$	$2.4x10^{-8}T^{-1}$	2	1119
7,7	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$3.0x10^{-12}$	3	1120
8,1	$H_2O_2 + M \rightarrow 2OH + M$	$10^{9.33}T^{-4.86}exp(-26795/T)$ >500 K <10 atm ($M=N_2$)	2	1120
8,3	$H_2O_2 + O_2 \rightarrow 2HO_2$	$9.0x10^{-11}exp(-20000/T)$	5	1121
8,4	$H_2O_2 + H \rightarrow H_2 + HO_2$ (a)	$8.0x10^{-11}exp(-4000/T)$	1.25 at 300 K, 2 at 773K, 5 at 1000 K	1122
	$\rightarrow H_2O + OH$ (b)	$4.0x10^{-11}exp(-2000/T)$		
8,5	$H_2O_2 + O \rightarrow OH + HO_2$	$1.6x10^{-17}T^2exp(-2000/T)$	3	1122
8,6	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$2.9x10^{-12}exp(-160/T)$	1.25 to 460 K, 3 (T>1000 K)	1123
9,1	$H_2O + M \rightarrow H + OH + M$	$5.8x10^{-9}exp(-52900/T)$ 2000-6000 K ($M=N_2$)	1.5	1124
9,4	$H_2O + H \rightarrow H_2 + OH$	$1.03x10^{-16}T^{1.9}exp(-9265/T)$	2.5	1124
9,5	$H_2O + O \rightarrow 2OH$	$7.6x10^{-15}T^{1.3}exp(-8605/T)$	2.5	1125
10,1	$CH_4 \rightarrow CH_3 + H$	$10^{15.57}exp(-52246/T)s^{-1}$ high pressure limit, 300-2500 K $log\ k/k\infty = 0.275-8.75x10^{-4}T$ $-7.11x10^{-8}T^2$ 1 atm, 1300-2500 K ($M=N_2$)	1.5	1125
10,3	$CH_4 + O_2 \rightarrow CH_3 + HO_2$	$6.7x10^{-11}exp(-28640/T)$	5	1128

Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant k/cm^3 $molecule^{-1}s^{-1}$	Uncertainty factor	Page
10,4	$CH_4 + H \rightarrow CH_3 + H_2$	$3.73x10^{-20}T^3exp(-4406/T)$	1.3 (500-800 K), 3 at 2500 K	1128
10,5	$CH_4 + O \rightarrow CH_3 + OH$	$1.7x10^{-15}T^{1.5}exp(-4330/T)$	1.25	1129
10,6	$CH_4 + OH \rightarrow CH_3 + H_2O$	$3.2x10^{-19}T^{2.4}exp(-1060/T)$	1.4	1130
10,7	$CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$	$3.0x10^{-13}exp(-9350/T)$	5	1131
11,1	$C_2H_6 \rightarrow 2CH_3$	$10^{22.5}T^{-1.79}exp(-45834/T)s^{-1}$ high pressure limit $log\ k/k\infty = -0.235+1.03x10^{-4}T$ $-1.11x10^{-6}T^2+1.425x10^{-10}T^3$ 800-2500 K, 1 atm (M=Ar)	1.5 2	1131
11,3	$C_2H_6 + O_2 \rightarrow C_2H_5 + HO_2$	$6.7x10^{-11}exp(-25600/T)$	5	1133
11,4	$C_2H_6 + H \rightarrow C_2H_5 + H_2$	$9.2x10^{-22}T^{3.5}exp(-2600/T)$	1.5 (T<1000 K), 3 at 2500 K	1134
11,5	$C_2H_6 + O \rightarrow C_2H_5 + OH$	$2.0x10^{-12}T^{0.6}exp(-3680/T)$	2	1134
11,6	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$1.47x10^{-14}T^{1.04}exp(-913/T)$	1.25 at 300 K, 2 at 2000 K	1135
11,7	$C_2H_6 + HO_2 \rightarrow H_2O_2 + C_2H_5$	$4.9x10^{-13}exp(-7520/T)$	3	1136
12,1	$HCHO + M \rightarrow H + HCO + M$	$10^{17.3}T^{-6.9}exp(-48590/T)$ 1000-3000 K (M=Ar)	3	1136
12,3	$HCHO + O_2 \rightarrow HO_2 + CHO$	$3.4x10^{-11}exp(-19600/T)$	2	1138
12,4	$HCHO + H \rightarrow H_2 + CHO$	$3.64x10^{-16}T^{1.77}exp(-1510/T)$	1.3 to 500 K, 3 at 2500 K	1138
12,5	$HCHO + O \rightarrow CHO + OH$	$3.0x10^{-11}exp(-1550/T)$	1.5 to 750 K	1139
12,6	$HCHO + OH \rightarrow HCO + H_2O$	$5.7x10^{-15}T^{1.18}exp(225/T)$	1.25 at 300 K, 2 at 1600 K	1140
12,7	$HCHO + HO_2 \rightarrow H_2O_2 + CHO$	$3.3x10^{-12}exp(-5870/T)$	3	1140
13,4	$CO_2 + H \rightarrow CO + OH$	$2.5x10^{-10}exp(-13300/T)$	1.2	1141

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No.	Reaction	Rate Constant k/cm^3 molecule^{-1}s^{-1}	Uncertainty factor	Page
13,5	$CO_2 + O \rightarrow CO + O_2$	2.8×10^{-11}exp(-26500/T)	2	1141
14,3	$CO + O_2 \rightarrow CO_2 + O$	4.2×10^{-12}exp(-24000/T	2	1142
14,4	$CO + H + M \rightarrow CHO + M$	$1.74\times10^{-27}T^{-1.82}$exp(-1856/T) cm^{6}molecule^{-2}s^{-1} 800-2500 K ($M=N_2$)	3	1142
14,5	$CO + O + M \rightarrow CO_2 + M$	1.7×10^{-33}exp(-1510/T) cm^{6}molecule^{-2}s^{-1} ($M=N_2$)	2.5	1144
14,6	$CO + OH \rightarrow H + CO_2$	1.12×10^{-13}exp(0.00091xT)	1.5	1144
14,7	$CO + HO_2 \rightarrow HO + CO_2$	2.5×10^{-10}exp(-11900/T)	3	1145
15,1	$CHO + M \rightarrow H + CO + M$	$8.5\times10^{-3}T^{-2.14}$exp(-10278/T)	5	1146
15,2	$CHO + H_2 \rightarrow HCHO + H$	$3.0\times10^{-18}T^2$exp(-8972/T)	5	1147
15,3	$HCO + O_2 \rightarrow HO_2 + CO$	8.5×10^{-11}exp(-850/T)	1.5 at 300 K, 5 at 1500 K	1147
15,4	$HCO + H \rightarrow H_2 + CO$	2.0×10^{-10}	2	1148
15,5	$CHO + O \rightarrow H + CO_2$ (a) $\rightarrow OH + CO$ (b)	$\sim5.0\times10^{-11}$ 5.0×10^{-11}	3	1149
15,6	$HCO + OH \rightarrow H_2O + CO$	$\sim5.0\times10^{-11}$	3	1149
15,7	$HCO + HO_2 \rightarrow OH + H + CO_2$	$\sim5.0\times10^{-11}$	5	1149
15,8	$HCO + H_2O_2 \rightarrow H_2CO + HO_2$	1.7×10^{-13}exp(-3486/T)	5	1149
15,9	$HCO + H_2O \rightarrow H_2CO + OH$	$3.9\times10^{-16}T^{1.35}$exp(-13146/T)	5	1150
15,10	$HCO + CH_4 \rightarrow CH_3 + HCHO$	$1.21\times10^{-20}T^{2.85}$exp(-11330/T)	5	1150
15,11	$HCO + C_2H_6 \rightarrow H_2CO + C_2H_5$	$7.8\times10^{-20}T^{2.72}$exp(-9176/T)	5	1150
15,15	$HCO + HCO \rightarrow H_2CO + CO$ (a) $\rightarrow H_2 + 2CO$ (b)	3.0×10^{-11} 5.0×10^{-12}	1.5 1.5	1151
16,2	$CH_3 + H_2 \rightarrow CH_4$	$4.8\times10^{-22}T^{3.12}$exp(-4384/T)	1.5 to 700 K, incr. to 3 at 2500 K	1152

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No.	Reaction	Rate Constant k/cm^3 $molecule^{-1}s^{-1}$	Uncertainty factor	Page
16,3	$CH_3 + O_2 \rightarrow CH_3O_2$ (a)	$1.5\times10^{35}T^{-15.01}\exp(-8567/T)$ 700-2500 K	3	1153
	$\rightarrow CH_3O + O$ (b)	$3.3\times10^{-6}T^{-1.57}\exp(-14710/T)$	3	
16,4	$CH_3 + H \rightarrow CH_4$	$2\times10^{-9}T^{-0.4}$ high pressure limit	1.5	1156
		$\log(k/k\infty)=0.275-8.75\times10^{-4}T-7.10\times10^{-8}T^2$ 1200-1500 K, 1 atm ($M=N_2$)	2	
16,5	$CH_3 + O \rightarrow HCHO + H$	1.3×10^{-10}	1.3	1159
16,6	$CH_3 + OH \rightarrow CH_3OH$ (a)	$k_a + k_b \simeq 9.0\times10^{-11}$ at 1 atm ($M=N_2$)	2	1159
	$\rightarrow CH_2O + H + H$ (b)	$k_b/k_a = 10^{-19.7}T^{6.4}\exp(-20/T)$ at 1 atm ($M=N_2$)	4	
16,7	$CH_3 + HO_2 \rightarrow CH_3O + OH$ (a)	3.3×10^{-11}	3	1162
	$\rightarrow CH_4 + O_2$ (b)	6.0×10^{-12}	5	
16,8	$CH_3 + H_2O_2 \rightarrow CH_4 + HO_2$	$2.0\times10^{-14}\exp(300/T)$	5	1162
16,9	$CH_3 + H_2O \rightarrow CH_4 + OH$	$8.0\times10^{-22}T^{2.9}\exp(-7480/T)$	1.6	1163
16,11	$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	$9.1\times10^{-25}T^4\exp(-4169/T)$	1.3 at 300 K, incr. to 3 at 2500 K	1163
16,12	$CH_3 + HCHO \rightarrow CH_4 + CHO$	$9.2\times10^{-21}T^{2.81}\exp(-2950/T)$	2 at 1000 K, incr. to 3 at 2510 K	1164
16,14	$CH_3 + CO + M \rightarrow CH_3CO + M$	$10^{-9.4}T^{-7.56}\exp(-5490/T)$ $cm^6molecule^{-2}s^{-1}$, ($M=N_2$) low pressure limit $\log(k(N_2, 1)/k_2(N_2, 0)) = -0.536$ $-8.68\times10^{-4}T-3.34\times10^{-7}T^2$ 700-2500 K, 1 atm ($M=N_2$)	3	1165
16,15	$CH_3 + CHO \rightarrow CH_4 + CO$ (a)	2.0×10^{-10}	2	1167
	$\rightarrow CH_3CO$ (b)	3.0×10^{-11}	2	
16,16	$2CH_3 \rightarrow C_2H_6$	$1.68\times10^{-9}T^{-0.64}$ high pressure limit $\log(k(Ar, 1\ atm)/k\infty) = -0.235$ $+1.033\times10^{-3}T-1.113\times10^{-6}T^2$ $+1.425\times10^{-10}T^3$ 700-2500 K, 1 atm ($M=N_2$)	1.1 at 300 K, 2 at 1400 K	1168

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No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
17,1	$C_2H_5 + M \rightarrow C_2H_4 + H + M$	$4.9x10^{9}T^{1.19}exp(-18722/T)s^{-1}$ high pressure limit $log(k(N_2,\ 1)/k\infty) = -0.236+1.35x10^{-3}T$ $-1.99x10^{-6}T^2+3.44x10^{-10}T^3$ 700-2500 K, 1 atm ($M=N_2$)	2	1170
17,2	$C_2H_5 + H_2 \rightarrow C_2H_6 + H$	$5.1x10^{-24}T^{3.6}exp(-4253/T)$	1.5 to 700 K, <4 at 1200 K	1172
17,3	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ (a)	$1.4x10^{-12}exp(-1950/T)$	1.5 at 800 K	1173
	$\rightarrow C_2H_4 + OH$ (b)	$1.0x10^{-13}exp(-3450/T)$		
17,4	$C_2H_5 + H \rightarrow C_2H_6$ (a)	$k_a + k_b = 6.0x10^{-11}$	3	1174
	$\rightarrow CH_3 + CH_3$ (b)	$log(k_b/k_a) = -1.915+2.69x10^{-3}T$ $-2.35x10^{-7}T^2$ 700-2500 K, 1 atm ($M=N_2$)		
	$\rightarrow C_2H_4 + H_2$ (c)	$3.0x10^{-12}$	3	
17,5	$C_2H_5 + O \rightarrow CH_3CHO + H$ (a)	$k_a + k_b = 1.6\ x\ 10^{-10}$	2	1175
	$\rightarrow HCHO + CH_3$ (b)	$k_a/k_b = 5 \pm 1$		
17,6	$C_2H_5 + OH \rightarrow C_2H_4 + H_2O$ (a)	$4.0x10^{-11}$	4	1176
	$\rightarrow CH_3 + H + HCHO$ (b)	$4.0x10^{11}$		
17,7	$C_2H_5 + HO_2 \rightarrow CH_3 + H_2CO + OH$ (a)	$4.0x10^{-11}$		1176
	$\rightarrow C_2H_6 + O_2$ (b)	$5.0x10^{-13}$		
	$\rightarrow C_2H_4 + H_2O_2$ (c)	$5.0x10^{-13}$		
17,8	$C_2H_5 + H_2O_2 \rightarrow C_2H_6 + HO_2$	$1.45x10^{-14}exp(-490/T)$	5	1177
17,9	$C_2H_5 + H_2O \rightarrow C_2H_6 + OH$	$5.6x10^{-18}T^{1.44}exp(-10150/T)$	2	1177
17,10	$C_2H_5 + CH_4 \rightarrow C_2H_6 + CH_3$	$1.4310^{-25}T^{4.14}exp(-6322/T)$	2	1177
17,12	$C_2H_5 + HCHO \rightarrow C_2H_6 + CHO$	$9.12x10^{-21}T^{2.81}exp(-2950/T)$	2 to 1000 K, incr. to 5 at 2500 K	1178
17,14	$C_2H_5 + CO \rightarrow C_2H_5CO$	$2.5x10^{-13}exp(-2420/T)/s$ high pressure limit $log(k(N_2,\ 1)/k\infty) = -0.181$ $+1.38x10^{-3}T-2.66x10^{-6}T^2$ 700-2500 K, 1 atm ($M=N_2$)	2	1178

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No.	Reaction	Rate Constant $k/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\mathrm{s}^{-1}$	Uncertainty factor	Page
17,15	$C_2H_5 + HCO \rightarrow C_2H_6 + CO$ (a)	$2.0\mathrm{x}10^{-10}$	3	1179
	$\rightarrow C_2H_5CHO$ (b)	$3.0\mathrm{x}10^{-11}$		
17,16	$C_2H_5 + CH_3 \rightarrow C_3H_8$ (a)	$4.7\mathrm{x}10^{-11}(300/T)^{0.5}$	1.3	1180
		high pressure limit		
		$\log(k_a/k_a(\infty)) = -0.318+1.14\mathrm{x}10^{-3}T$		
		$-8.35\mathrm{x}10^{-7}T^2-2.16\mathrm{x}10^{-11}T^3$	2	
		700-2500 K, 1 atm ($M=N_2$)		
	$\rightarrow CH_4 + C_2H_4$ (b)	$0.04\ k_a(\infty)$		
17,17	$C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ (a)	$1.8\mathrm{x}10^{-11}$	1.2	1181
	$\rightarrow C_2H_4 + C_2H_6$ (b)	$0.23\mathrm{x}10^{-11}$	1.2	
18,1	$C_2H_4 \rightarrow C_2H_2 + H_2$	$10^{12.9}T^{0.44}\exp(-44670/T)\mathrm{s}^{-1}$	3	1182
		$\log(k/k\infty) = 0.44-2.09\mathrm{x}10^{-4}T$		
		$-2.66\mathrm{x}10^{-7}T^2$		
		at 1 atm from 1200-2500 K, ($M=N_2$)		
18,2	$C_2H_4 + H_2 \rightarrow C_2H_5 + H$	$1.7\mathrm{x}10^{-11}\exp(-34300/T)$	3	1184
18,3	$C_2H_4 + O_2 \rightarrow C_2H_4 + HO_2$	$7.0\mathrm{x}10^{-11}\exp(-29000/T)$	10	1184
18,4	$C_2H_4 + H \rightarrow C_2H_5$ (a)	$1.4\mathrm{x}10^{-15}T^{1.49}\exp(-499/T)$	1.3 to 900 K	1185
		high pressure limit		
		$\log(k/k\infty) = -0.236+1.35\mathrm{x}10^{-3}T$	3	
		$-1.99\mathrm{x}10^{-6}T^2+3.44\mathrm{x}10^{-10}T^3$		
		700-2000 K, 1 atm ($M=N_2$)		
	$\rightarrow C_2H_3 + H_2$ (b)	$2.2\mathrm{x}10^{-18}T^{2.53}\exp(-6160/T)$		
18,5	$C_2H_4 + O \rightarrow CH_3 + HCO$	$2.2\mathrm{x}10^{-16}T^{1.55}\exp(-215/T)$	1.2 to 940 K, 2 at higher temp.	1187
18,6	$C_2H_4 + OH \rightarrow C_2H_3 + H_2O$ (a)	$2.6\mathrm{x}10^{-20}T^{2.75}\exp(-2100/T)$	10	1189
	$C_2H_4 + OH(+M) \rightarrow C_2H_4OH(+M)$ (b)	$9.0\mathrm{x}10^{-12}$		
18,7	$C_2H_4 + HO_2 \rightarrow CH_3CHO + OH$	$1.0\mathrm{x}10^{-14}\exp(-4000/T)$	3 at 773K, 10 at higher and lower T	1189
18,14	$C_2H_4 + CO \rightarrow C_2H_3 + HCO$	$2.5\mathrm{x}10^{-10}\exp(-45600/T)$	5	1190

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18,16	$C_2H_4 + CH_3 \rightarrow C_2H_3 + CH_4$ (a) $C_2H_4 + CH_3 \rightarrow nC_3H_7$ (b)	$1.1x10^{-23}T^{3.7}exp(-4780/T)$ $5.5x10^{-13}exp(-3877/T)$ high pressure limit process is reversed at high temperatures	2 1.3	1191
18,17	$C_2H_4 + C_2H_5 \rightarrow C_2H_6 + C_2H_3$	$1.05x10^{-21}T^{3.13}exp(-9063/T)$	10	1191
18,18	$C_2H_4 + C_2H_4 \rightarrow C_2H_3 + C_2H_5$	$8.0x10^{-10}exp(-36000/T)$	10	1192
19,1	$C_2H_3 + M \rightarrow C_2H_2 + H + M$	$6.9x10^{17}T^{-7.49}exp(-22917/T)$ low pressure limit with N_2 $log(k/k_o) = -3.00+4.68x10^{-3}T$ $-2.51x10^{-6}T^2+4.50x10^{-10}T^3$ 1 atm ($M=N_2$) >700 K	10	1193
19,2	$C_2H_3 + H_2 \rightarrow C_2H_4 + H$	$5.0x10^{-20}T^{2.63}exp(-4298/T)$	10	1195
19,3	$C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$	$2.0x10^{-13}$	5	1195
19,4	$C_2H_3 + H \rightarrow C_2H_2 + H_2$	$1.6x10^{-10}$	2.5	1195
19,5	$C_2H_3 + O \rightarrow CH_2CO + H$	$1.6x10^{-10}$	3	1195
19,6	$C_2H_3 + OH \rightarrow H_2O + C_2H_2$ (a) $\rightarrow CH_3CHO$ (b)	$5.0x10^{-11}$ $5.0x10^{-11}$	3 3	1196
19,7	$C_2H_3 + HO_2 \rightarrow OH + CH_3 + CO$	$5.0x10^{-11}$	3	1196
19,8	$C_2H_3 + H_2O_2 \rightarrow C_2H_4 + HO_2$	$2.0x10^{-14}exp(300/T)$	10	1196
19,9	$C_2H_3 + H_2O \rightarrow C_2H_4 + OH$	$8.0x10^{-22}T^{2.9}exp(-7480/T)$	5 at T>1000 K, larger at lower temp.	1196
19,10	$C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3$	$2.4x10^{-24}T^{4.02}exp(-2754/T)$	5 at T>1000 K, larger at lower temp.	1197
19,11	$C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5$	$1.0x10^{-21}T^{3.3}exp(-5285/T)$	5 at T>1000 K, larger at lower temp.	1197

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No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
19,12	$C_2H_3 + HCHO \rightarrow C_2H_4 + CHO$	$9.0\times10^{-21}T^{2.81}\exp(-2950/T)$	5 at T>1000 K, larger at lower temp.	1197
19,14	$C_2H_3 + CO \rightarrow C_2H_3CO$	$2.5\times10^{-13}\exp(-2420/T)$ high pressure limit $\log(k/k\infty) = -0.34+1.58\times10^{-3}T$ $-1.85\times10^{-6}T^2+2.79\times10^{-10}T^3$ at 1 atm ($M=N_2$), 700-1500 K	5	1198
19,15	$C_2H_3 + HCO \rightarrow C_2H_4 + CO$ (a)	1.5×10^{-10}	3	1199
	$\rightarrow C_2H_3CHO$ (b)	3.0×10^{-11}	3	
19,16	$C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4$ (a)	6.5×10^{-13}	3	1200
	$\rightarrow C_3H_5 + H$ (b)	$k_b+k_c = 4.2\times10^{-11}$ high pressure limit	2	
	$\rightarrow C_3H_6$ (c)	$\log(k_b+k_c)/(k_b+k_c)\infty = -0.177$ $+6.69\times10^{-4}T-6.04\times10^{-7}T^2$ $+1.07\times10^{-10}T^3$ $k_b/k_c=1.1\times10^{-28}T^{8.52}\exp(1248/T)$ at 1 atm ($M=N_2$), 700-2500 K		
19,17	$C_2H_3 + C_2H_5 \rightarrow 1\text{-}C_4H_8$ (a)	$k_a+k_b = 2.5\times10^{-11}$ under all pressure and temp. conditions	2	1202
	$\rightarrow C_3H_5 + CH_3$ (b)	$k_b/k_a=2.5\times10^{-36}T^{11.25}\exp(3289/T)$ at 1 atm, 700-2500 K	5	
	$\rightarrow 2C_2H_4$	0.8×10^{-12}	3	
	$\rightarrow C_2H_2 + C_2H_6$	0.8×10^{-12}	3	
19,18	$C_2H_3 + C_2H_4 \rightarrow C_4H_6 + H$	$8.3\times10^{-13}\exp(-3676/T)$	10	1204
19,19	$C_2H_3 + C_2H_3 \rightarrow C_4H_6$ (a)	$k_a+k_c = 1.6\times10^{-11}$	2	1204
	$\rightarrow C_2H_4 + C_2H_2$ (b)	high pressure limit		
	$\rightarrow C_4H_5 + H$ (c)	$\log((k_a+k_c)/(k_a+k_c)\infty = -0.04$ $+1.04\times10^{-4}T-5.42\times10^{-9}T^2$ $-5.07\times10^{-11}T^3$ $k_c/k_a = 1.3\times10^{-27}T^{8.07}\exp(+1315/T)$ at 1 atm ($M=N_2$) from 700-2500 K		
		$k_b = 1.6\times10^{-12}$	5	

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20,1	$C_2H_2 \rightarrow C_2H + H$	$10^{15.42}exp(-62445/T)s^{-1}$ $\log(k/k\infty) - 0.178-3.966\times10^{-4}T$ $-1.331\times10^{-7}T^2$ 1 atm ($M=N_2$) from 700-2500 K	1.5	1207
20,2	$C_2H_2 + H_2 \rightarrow C_2H_4$ (a)	$5.0\times10^{-13}exp(-19600/T)$ $\log(k/k\infty) = 0.44-2.09\times10^{-4}T$ $-2.66\times10^{-7}T^2$	3	1209
	$\rightarrow C_2H_3 + H$ (b)	$4.0\times10^{-12}exp(-32700/T)$	10	
20,3	$C_2H_2 + O_2 \rightarrow C_2H + HO_2$	$2.0\times10^{-11}exp(-37500/T)$	10	1209
20,4	$C_2H_2 + H + M \rightarrow C_2H_3 + M$ (a)	$1.05\times10^{-7}T^{-7.27}exp(-3632/T)$ $cm^6molecule^{-2}s^{-1}$ limiting low pressure expression in N_2 for 700-2500 K	2	1210
		$\log(k/k(o)) = -3.0+4.68\times10^{-3}T$ $-2.51\times10^{-6}T^2+4.50\times10^{-10}T^3$ 1 atm ($M=N_2$) 700-2510 K	2	
	$\rightarrow C_2H + H_2$ (b)	$10^{-10}exp(-11200/T)$		
20,5	$C_2H_2 + O \rightarrow CH_2 + CO$ (a)	$k_a+k_b = 2.9\times10^{-11}exp(-1600/T)$	1.5 to 600 K, incr. to 5 at 2500 K	1212
	$\rightarrow C_2HO + H$ (b)	$k_b = 1.5\times10^{-11}exp(-2285/T)$		
20,6	$C_2H_2 + OH \rightarrow C_2H + H_2O$	$2.4\times10^{-20}T^{2.68}exp(-6060/T)$	10	1213
20,7	$C_2H_2 + HO_2 \rightarrow CH_2{=}C{=}O + OH$	$1.0\times10^{-14}exp(-4000/T)$	10	1214
20,14	$C_2H_2 + CO \rightarrow C_2H + CHO$	$8.0\times10^{-10}exp(-53700/T)$	10	1214
20,16	$C_2H_2 + CH_3 \rightarrow C_3H_5$ (a)	$1.0\times10^{-12}exp(-3877/T)$ process is reversed at higher temperatures	1.3	1214
	$\rightarrow CH_4 + C_2H$ (b)	$3.0\times10^{-13}exp(-8700/T)$	5	
20,17	$C_2H_2 + C_2H_5 \rightarrow C_2H + C_2H_6$	$4.5\times10^{-13}exp(-11800/T)$	5	1215
20,18	$C_2H_2 + C_2H_4 \rightarrow 2C_2H_3$	$4.0\times10^{-11}exp(-34400/T)$	10	1215
20,20	$C_2H_2 + C_2H_2 \rightarrow C_2H_3 + C_2H$	$1.6\times10^{-11}exp(-42500/T)$	5	1215

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21,2	$C_2H + H_2 \rightarrow C_2H_2 + H$	$1.9\times10^{-11}\exp(-1450/T)$	1.3 at 300 K, incr. to 3 at 2500 K	1216
21,3	$C_2H + O_2 \rightarrow CO + HCO$ (a)	4×10^{-12}	1.3 at 300 K, incr. to 10 at 2500 K	1217
	$\rightarrow HC_2O + O$ (b)	1×10^{-12}		
21,4	$C_2H + H \rightarrow C_2H_2$ (a)	3.0×10^{-10}	1.5	1218
		high pressure limit $\log(k/k_\infty) = 0.005+7.85\times10^{-5}T -1.77\times10^{-7}T^2$ $(M=N_2)$ at 1 atm, 700-2500 K	2	
	$\rightarrow C_2 + H_2$ (b)	$6.0\times10^{-11}\exp(-14223/T)$	10	
21,5	$C_2H + O \rightarrow CH + CO$	3.0×10^{-11}	3	1219
21,6	$C_2H + OH \rightarrow C_2H_2 + O$ (a)	3.0×10^{-11}	10	1219
	$\rightarrow CH_2 + CO$ (b)	3.0×10^{-11}	10	
21,7	$C_2H + HO_2 \rightarrow C_2H_2 + O_2$	3.0×10^{-11}	10	1219
	$\rightarrow HC_2O + OH$	3.0×10^{-11}	10	
21,10	$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$	$3.0\times10^{-12}\exp(-250/T)$	1.3 at 300 K, incr. to 3 at 2500 K	1220
21,11	$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$	6.0×10^{-12}	1.3 at 300 K, incr. to 3 at 2500 K	1221
21,14	$C_2H + CO \rightarrow C_2HCO$	$2.5\times10^{-13}\exp(-2420/T)$ reaction reversed at high temperatures	10	1221
21,15	$C_2H + HCO \rightarrow C_2H_2 + CO$	1.0×10^{-10}	3	1222
21,16	$C_2H + CH_3 \rightarrow C_3H_3 + H$	4.0×10^{-11}	3	1222
21,17	$C_2H + C_2H_5 \rightarrow C_2H_2 + C_2H_4$ (a)	3.0×10^{-12}	3	1222
	$\rightarrow C_3H_3 + CH_3$ (b)	3.0×10^{-11}	3	
21,18	$C_2H + C_2H_4 \rightarrow C_4H_4 + H$	2.0×10^{-11}	3	1222

Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant k/cm^3 $molecule^{-1}s^{-1}$	Uncertainty factor	Page
21,19	$C_2H + C_2H_3 \rightarrow C_4H_4$ (a)	$k_a+k_b = 3.0\times10^{-11}$	2	1223
	$\rightarrow C_4H_3 + H$ (b)	$k_b/k_a = 9.5\times10^{-20}T^{6.23}\exp(1660/T)$ $(M=N_2)$ at 1 atm, 700-2500 K	3	
	$\rightarrow C_2H_2 + C_2H_2$ (c)	1.6×10^{-12}	3	
21,20	$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	4.0×10^{-11}	1.2	1224
21,21	$C_2H + C_2H \rightarrow C_4H_2$ (a)	$k_a+k_b = 3.0\times10^{-11}$	2	1225
	$\rightarrow C_4H + H$ (b)	$k_b/k_a = 8.3\times10^{-17}T^{5.25}\exp(1611/T)$ $(M=N_2)$ at 1 atm, 700-2500 K		
	$\rightarrow C_2H_2 + C_2$	3.0×10^{-12}	3	
22,1	$CH_3CO + M \rightarrow CH_3 + CO + M$	$1.45\times10^{19}T^{-8.62}\exp(-11284/T)$ limiting low pressure rate for N_2, 500-2500 K $\log k/k_o = -0.54+8.68\times10^{-4}T$ $-3.34\times10^{-7}T^2$	2	1226
22,2	$CH_3CO + H_2 \rightarrow CH_3CHO + H$	$6.8\times10^{-18}T^{1.82}\exp(-8862/T)$	3	1229
22,3	$CH_3CO + O_2 \rightarrow CH_3COO_2$	3.0×10^{-12} reaction reversed at at high temperatures	2	1229
22,4	$CH_3CO + H \rightarrow CH_3 + HCO$	1.6×10^{-10}	3	1230
22,5	$CH_3CO + O \rightarrow CH_3 + CO_2$	1.6×10^{-11}	3	1230
22,6	$CH_3CO + OH \rightarrow CH_2CO + H_2O$ (a)	2.0×10^{-11}	3	1230
	$\rightarrow CH_3 + CO + OH$ (b)	5.0×10^{-11}	3	
22,7	$CH_3CO + HO_2 \rightarrow CH_3 + CO_2 + OH$	5.0×10^{-11}	3	1230
22,8	$CH_3CO + H_2O_2 \rightarrow CH_3CHO + HO_2$	$3.0\times10^{-13}\exp(-4140/T)$	5	1231
22,10	$CH_3CO + CH_4 \rightarrow CH_3CHO + CH_3$	$3.6\times10^{-21}T^{2.88}\exp(-10800/T)$	5	1231
22,11	$CH_3CO + C_2H_6 + C_2H_5 + CH_3CHO$	$3.0\times10^{-20}T^{2.75}\exp(-8820/T)$	5	1231
22,12	$CH_3CO + HCHO \rightarrow CH_3CHO + CHO$	$3.0\times10^{-13}\exp(-6500/T)$	10	1231
22,15	$CH_3CO + CHO \rightarrow CH_3CHO + CO$ (a)	1.5×10^{-11}	3	1232
	$\rightarrow CH_3COCHO$ (b)	3.0×10^{-11}	3	

Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
22,16	$CH_3CO + CH_3 \rightarrow CH_3COCH_3$	$6.7\times10^{-9}T^{-0.8}$	1.5	1232
		high pressure limit $\log(k/k_\infty) = -0.44+1.80\times10^{-3}T$ $-1.7\times10^{-6}T^2+1.93\times10^{-10}T^3$	2	
22,17	$CH_3CO + C_2H_5 \rightarrow C_2H_5COCH_3$	$5.19\times10^{-10}T^{-0.5}$	2	1234
22,19	$CH_3CO + C_2H_3 \rightarrow CH_3 + COC_2H_3$	3.0×10^{-11}	3	1234
22,21	$CH_3CO + C_2H \rightarrow C_2HCO + CH_3$	3.0×10^{-11}	3	1234
22,22	$CH_3CO + CH_3CO \rightarrow CH_3COCOCH_3$	2.0×10^{-11}	2	1234
23,1	$CH_3O_2 + M \rightarrow CH_3 + O_2 + M$	$1.2\times10^{25}T^{-10.02}\exp(-16731/T)$	3	1235
		limiting low pressure rate $\log(k/k_0) = -2.54+4.6\times10^{-3}T$ $-2.69\times10^{-6}T^2+5.06\times10^{-10}T^3$ 1 atm ($M=N_2$), 700-1500 K	2	
23,2	$CH_3O_2 + H_2 \rightarrow CH_3O_2H + H$	$5.0\times10^{-11}\exp(-13100/T)$	10	1237
23,4	$CH_3O_2 + H \rightarrow CH_3O + OH$	1.6×10^{-10}	3	1237
23,5	$CH_3O_2 + O \rightarrow CH_3O + O_2$	6.0×10^{-11}	5	1237
23,6	$CH_3O_2 + OH \rightarrow CH_3OH + O_2$	1.0×10^{-10}	5	1238
23,7	$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$	$7.7\times10^{-14}\exp(+1300/T)$	5	1238
23,8	$CH_3O_2 + H_2O_2 \rightarrow CH_3OOH + HO_2$	$4.0\times10^{-12}\exp(-5000/T)$	10	1238
23,10	$CH_3O_2 + CH_4 \rightarrow CH_3OOH + CH_3$	$3.0\times10^{-13}\exp(-9300/T)$	10	1239
23,11	$CH_3O_2 + C_2H_6 \rightarrow CH_3O_2H + C_2H_5$	$4.9\times10^{-13}\exp(-7520/T)$	10	1239
23,12	$CH_3O_2 + HCHO \rightarrow CH_3O_2H + CHO$	$3.3\times10^{-12}\exp(-5870/T)$	10	1239
23,15	$CH_3O_2 + HCO \rightarrow CH_3O + H + CO_2$	5.0×10^{-11}	3	1239
23,16	$CH_3O_2 + CH_3 \rightarrow 2CH_3O$	4.0×10^{-11}	3	1240
23,17	$CH_3O_2 + C_2H_5 \rightarrow CH_3O + C_2H_5O$	4.0×10^{-11}	3	1240
23,19	$CH_3O_2 + C_2H_3 \rightarrow CH_3O + C_2H_3O$	4.0×10^{-11}	3	1240

Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant k/cm^3 $molecule^{-1}s^{-1}$	Uncertainty factor	Page
23,21	$CH_3O_2 + C_2H \rightarrow CH_3O + HC_2O$	$4.0x10^{-11}$	3	1240
23,22	$CH_3O_2 + CH_3CO \rightarrow CH_3 + CO_2 + CH_3O$	$4.0x10^{-11}$	3	1241
23,23	$2CH_3O_2 \rightarrow 2CH_3O + O_2$ (a) $\rightarrow CH_3OH + HCHO + O_2$ (b) $\rightarrow CH_3O_2CH_3 + O_2$ (c)	$1.3x10^{-13}$ $2.1x10^{-13}$ $<3.0x10^{-14}$	2 at 300 K, considerably larger at high temp.	1241
24,1	$CH_3O + M \rightarrow HCHO + H + M$	$6.5x10^{13}T^{-6.65}exp(-16740/T)$ $(M=N_2)$, 700-2500 K to 10 atm	4	1242
24,3	$CH_3O + O_2 \rightarrow HCHO + HO_2$	$1.1x10^{-13}(-1310/T)$	10 at 300 K, 2 (T>400 K)	1243
24,4	$CH_3O + H \rightarrow HCHO + H_2$	$3.3x10^{-11}$	3	1243
24,5	$CH_3O + O \rightarrow CH_2O + OH$	$1.0x10^{-11}$	5	1244
24,6	$CH_3O + OH \rightarrow CH_2O + H_2O$	$3.0x10^{-11}$	5	1244
24,7	$CH_3O + HO_2 \rightarrow CH_2O + H_2O_2$	$5.0x10^{-13}$	10	1244
24,10	$CH_3O + CH_4 \rightarrow CH_3OH + CH_3$	$2.6x10^{-13}exp(-4450/T)$	3	1244
24,11	$CH_3O + C_2H_6 \rightarrow CH_3OH + C_2H_5$	$4.0x10^{-13}exp(-3570/T)$	3	1245
24,12	$CH_3O + HCHO \rightarrow CH_3OH + HCO$	$1.7x10^{-13}exp(-1500/T)$	3	1245
24,14	$CH_3O + CO \rightarrow CH_3 + CO_2$	$2.6x10^{-11}exp(-5940/T)$	5	1246
24,15	$CH_3O + HCO \rightarrow CH_3OH + CO$	$1.5x10^{-10}$	3	1246
24,16	$CH_3O + CH_3 \rightarrow CH_3O + CH_4$ (a) $\rightarrow CH_3OCH_3$ (b)	$4.0x10^{-11}$ $2.0x10^{-11}$	5	1247
24,17	$CH_3O + C_2H_5 \rightarrow HCHO + C_2H_6$	$4.0x10^{-11}$	5	1247
24,18	$CH_3O + C_2H_4 \rightarrow$ products	$2.0x10^{-13}exp(-3400/T)$	10	1248
24,19	$CH_3O + C_2H_3 \rightarrow HCHO + C_2H_4$	$4.0x10^{-11}$	5	1248
24,20	$CH_3O + C_2H_2 \rightarrow$ products	$2.0x10^{-13}exp(-10000/T)$	10	1249

Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
24,21	$CH_3O + C_2H \rightarrow HCHO + C_2H_2$	$4.0x10^{-11}$	5	1249
24,22	$CH_3O + CH_3CO \rightarrow CH_3OH + CH_2CO$ (a)	$1.0x10^{-11}$	10	1250
	$\rightarrow HCHO + CH_3CHO$ (b)	$1.0x10^{-11}$	10	
24,23	$CH_3O + CH_3O_2 \rightarrow HCHO + CH_3OOH$	$5.0x10^{-13}$	10	1250
24,24	$CH_3O + CH_3O \rightarrow CH_3O + HCHO$ (a)	$1.0x10^{-10}$	5	1251
	$\rightarrow CH_3OOCH_3$ (b)	$3.0x10^{-12}$		
25,1	$^1CH_2 + N_2 \rightarrow {}^3CH_2 + N_2$	$1.0x10^{-11}$	1.3	1252
25,2	$^1CH_2 + H_2 \rightarrow CH_3 + H$	$1.2x10^{-10}$	1.3	1253
25,3	$^1CH_2 + O_2 \rightarrow$ products	$5.2x10^{-11}$	1.6	1253
25,4	$^1CH_2 + H \rightarrow CH + H_2$	$5.0x10^{-11}$	3	1254
25,5	$^1CH_2 + O \rightarrow CO + 2H$ (a)	$2.5x10^{-11}$	3	1255
	$\rightarrow CO + H_2$ (b)	$2.5x10^{-11}$	3	
25,6	$^1CH_2 + OH \rightarrow HCHO + H$	$5.0x10^{-11}$	3	1255
25,7	$^1CH_2 + HO_2 \rightarrow HCHO + OH$	$5.0x10^{-11}$	3	1255
25,8	$^1CH_2 + H_2O_2 \rightarrow CH_3O + OH$	$5.0x10^{-11}$	3	1255
25,9	$^1CH_2 + H_2O \rightarrow CH_3OH$	$3.0x10^{-11}$	3	1256
25,10	$^1CH_2 + CH_4 \rightarrow C_2H_6{}^* \rightarrow 2CH_3$	$7.1x10^{-11}$	1.5	1256
25,11	$^1CH_2 + C_2H_6 \rightarrow C_3H_8{}^* \rightarrow$ $CH_3 + C_2H_5$	$1.9x10^{-10}$	2	1257
25,12	$^1CH_2 + HCHO \rightarrow CH_3 + HCO$	$2.0x10^{-12}$	5	1258
25,13	$^1CH_2 + CO_2 \rightarrow$ products	$5.0x10^{-12}$	5	1258
25,14	$^1CH_2 + CO \rightarrow$ products	$5.2x10^{-11}$	1.4	1259
25,15	$^1CH_2 + HCO \rightarrow CH_3 + CO$	$3.0x10^{-11}$	3	1259
25,16	$^1CH_2 + CH_3 \rightarrow C_2H_4 + H$	$3.0x10^{-11}$	3	1260

Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant k/cm^3 molecule$^{-1}s^{-1}$	Uncertainty factor	Page
25,17	$^1CH_2 + C_2H_5 \rightarrow C_2H_4 + CH_3$ (a)	$1.5x10^{-11}$	3	1260
	$\rightarrow C_3H_6 + H$ (b)	$1.5x10^{-11}$	3	
25,18	$^1CH_2 + C_2H_4 \rightarrow C_3H_6$	$1.5x10^{-10}$	2	1260
25,19	$^1CH_2 + C_2H_3 \rightarrow C_2H_2 + CH_3$	$3.0x10^{-11}$	3	1261
25,20	$^1CH_2 + C_2H_2 \rightarrow C_3H_4$	$1.0x10^{-10}$	10	1261
25,21	$^1CH_2 + C_2H \rightarrow C_2H_2 + CH$	$3.0x10^{-11}$	3	1261
25,22	$^1CH_2 + CH_3CO \rightarrow CH_3 + CH_2CO$	$3.0x10^{-11}$	3	1262
25,23	$^1CH_2 + CH_2O_2 \rightarrow C_2H_5 + O_2$	$3.0x10^{-11}$	3	1262
25,24	$^1CH_2 + CH_3O \rightarrow CH_3 + HCHO$	$3.0x10^{-11}$	3	1262
25,25	$^1CH_2 + {}^1CH_2 \rightarrow$ products	$5.0x10^{-11}$	5	1262
26,1	$^3CH_2 + N_2 \rightarrow$ products	$<1.0x10^{-16}$		1263
26,2	$^3CH_2 + H_2 \rightarrow CH_3 + H$	$<5.0x10^{-15}$		1263
26,3	$^3CH_2 + O_2 \rightarrow H + CO + OH$ (a)	$1.0x10^{-12}$	2	1264
	$\rightarrow H_2O + CO$ (b)	$4.0x10^{-13}$	2	
26,4	$^3CH_2 + H \rightarrow CH + H_2$	$2.7x10^{-10}$	2	1265
26,5	$^3CH_2 + O \rightarrow CO(v>0) + 2H$ (a)	$1.0x10^{-11}$	2	1265
	$\rightarrow CO(v>0) + H_2$ (b)	$1.0x10^{-11}$	2	
26,6	$^3CH_2 + OH \rightarrow HCHO + H$	$3.0x10^{-11}$	3	1266
26,7	$^3CH_2 + HO_2 \rightarrow$ products	$3.0x10^{-11}$	3	1266
26,8	$^3CH_2 + H_2O_2 \rightarrow CH_3 + HO_2$	$<1x10^{-14}$		1266
26,9	$^3CH_2 + H_2O \rightarrow CH_3 + OH$	$<1x10^{-16}$		1266
26,10	$^3CH_2 + CH_4 \rightarrow CH_3 + CH_3$	$<3.0x10^{-19}$		1267
26,11	$^3CH_2 + C_2H_6 \rightarrow$ products	$<3.0x10^{-19}$		1267
26,12	$^3CH_2 + HCHO \rightarrow CH_3 + HCO$	$<1.0x10^{-14}$		1267

Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant k/cm^3 $molecule^{-1}s^{-1}$	Uncertainty factor	Page
26,13	$^3CH_2 + CO_2 \rightarrow HCHO + CO$	3.9×10^{-14}	1.6	1268
26,14	$^3CH_2 + CO \rightarrow CH_2CO$	$<1.0 \times 10^{-15}$		1268
26,15	$^3CH_2 + HCO \rightarrow CH_3 + CO$	3.0×10^{-11}	3	1269
26,16	$^3CH_2 + CH_3 \rightarrow C_2H_4 + H$	7.0×10^{-11}	2	1269
26,17	$^3CH_2 + C_2H_5 \rightarrow CH_3 + C_2H_4$	3.0×10^{-11}	3	1269
26,18	$^3CH_2 + C_2H_4 \rightarrow C_3H_6$	$<3.0 \times 10^{-14}$	3	1270
26,19	$^3CH_2 + C_2H_3 \rightarrow CH_3 + C_2H_2$	3.0×10^{-11}	3	1270
26,20	$^3CH_2 + C_2H_2 \rightarrow C_3H_4$	5.8×10^{-12}	2	1270
26,21	$^3CH_2 + C_2H \rightarrow CH + C_2H_2$	3.0×10^{-11}	3	1271
26,22	$^3CH_2 + CH_3O_2 \rightarrow CH_3 + CH_2CO$	3.0×10^{-11}	3	1271
26,23	$^3CH_2 + CH_3O_2 \rightarrow HCHO + CH_3O$	3.0×10^{-11}	3	1271
26,24	$^3CH_2 + CH_3O \rightarrow CH_3 + HCHO$	3.0×10^{-11}	3	1272
26,25	$^3CH_2 + {}^1CH_2 \rightarrow$ products	3.0×10^{-11}	3	1272
26.26	$^3CH_2 + {}^3CH_2 \rightarrow$ products	5.3×10^{-11}	3	1272

3. Chemical Kinetic Data Tables

2,1 $H_2 + M \rightarrow 2H + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Cohen, Westberg (1983) evaln.	600-2000		$7.6x10^{-5}T^{-1.4}exp(-52530/T)$ ($M=N_2$)	3
	600-5000		$9.7x10^{-6}T^{-1.1}exp(-52530/T)$ (M=Ar)	2
	600-2000		$1.4x10^{-4}T^{-1.1}exp(-52530/T)$ ($M=H_2O$)	10

Comments and Recommendations

This is a comprehensive review of an extensively studied system. Earlier results from more than 50 studies were critically evaluated by Baulch et al. (1972).

(R. F. Hampson, May 1983)

References

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

3,1 $O_2 + M \rightarrow O + O + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = 4.79 + 0.58 \log T - 26115/T$				
Baulch, et al. (1976) evaln.	3000-18000		$3.0x10^{-6}T^{-1}exp(-59380/T)$ (M=Ar)	2
			$16.3T^{-2.5}exp(-59380/T)$ ($M=O_2$)	2.5

Comments and Recommendations

This is a comprehensive review of an extensively studied system.

(R. F. Hampson, May 1983)

References

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reaction for the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-Containing Species," (Butterworths, London, 1976)

3,2 $O_2 + H_2 \rightarrow H + HO_2$

Comments and Recommendations

On the basis of the rate of the reverse reaction (7,4) $k(H + HO_2 \rightarrow H_2 + O_2)= 1.1\times10^{-10}\exp(-1070/T)\mathrm{cm^3molecule^{-1}s^{-1}}$ and thermodynamic data, we suggest $k=2.4\times10^{-10}\exp(-28500/T)\mathrm{cm^3molecule^{-1}s^{-1}}$ with an uncertainty of a factor of 5 for the temperature range 300-800 K. This expression has been adjusted from the expression in Baulch et al. (1972) to allow for newer thermochemistry for HO_2 and a different recommendation for k_{rev}. See that review for a discussion of earlier data.
(R. F. Hampson, May 1983)

References

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

4,3 $H + O_2 \rightarrow OH + O$ (a)
$H + O_2 + M \rightarrow HO_2 + M$ (b)

Reference	Conditions Temp./K	 [M]/molecule $\mathrm{cm^{-3}}$	Reaction rate constant, $\mathrm{k/cm^3molecule^{-1}s^{-1}}$	Uncertainty factor
Cohen, Westberg (1983) review	300-2500		$k_a=2.8\times10^{-7}T^{-0.9}\exp(-8750/T)$	1.3 for T>1250 K incr. to 2 at 300 K
CODATA (1984) evaln.	200-400		$k_b=5.9\times10^{-32}(300/T)^{-1.0}$ $\mathrm{cm^6molecule^{-2}s^{-1}}$ ($M=O_2$ N_2) ($M=O_2$, N_2)	1.3 at 298 K
NASA (1985) evaln.	200-300		$k_b=5.5\times10^{-32}(300/T)^{-1.6}$ $\mathrm{cm^6molecule^{-2}s^{-1}}$	

Comments and Recommendations

There have been numerous measurements of reaction rate (a) at temperatures greater than 780 K. The recommendation given in the comprehensive review of Cohen and Westberg is accepted. It is based on the most accurate of these and also on measurements of the reverse rate at lower temperatures and equilibrium constant data. Rate data for the low pressure three-body reaction (b) are discussed in CODATA(1984) and NASA(1985).
(R. F. Hampson, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data. 12, 531 (1983)
NASA(1985). Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation No. 7, NASA Panel for Data Evaluation, JPL Publication 85-37 July 1985

4,4 $H + H + M \rightarrow H_2 + M$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
$\log K_p = -2.84 - 0.9 \log T + 22815/T$				
Cohen, Westberg (1983) evaln.	77-2000		$1.5\times10^{-29}T^{-1.3}cm^6molecule^{-2}s^{-1}$ ($M=N_2$)	2
	77-5000		$1.9\times10^{-30}T^{-1}cm^6molecule^{-2}s^{-1}$ (M=Ar)	2
	300-2000		$2.8\times10^{-29}T^{-1}cm^6molecule^{-2}s^{-1}$ ($M=H_2O$)	10

Comments and Recommendations

The recommendations of Cohen and Westberg are based on low-temperature measurements of the hydrogen atom recombination reaction and shock tube studies of H_2 dissociation. Earlier results were critically evaluated by Baulch et al. (1972).

It should be noted that H_2O is a much more efficient third body than Ar by a factor of approximately 15.
(R. F. Hampson, May 1983)

References

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)
Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

5,2 $O + H_2 \rightarrow OH + H$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	$[M]$/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Cohen, Westberg (1983) review	300-2500		$1.8x10^{-20}T^{2.8}exp(-2980/T)$	1.6 for T=400-1000 K incr. to 2 at 1600 K

Comments and Recommendations

There have been numerous studies of this reaction rate. The recommendation given in the comprehensive review by Cohen and Westberg is based on the most accurate of these and is accepted.

(R. F. Hampson, May 1983)

References

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

5,4 $O + H + M \rightarrow OH + M$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	$[M]$/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Baulch, et al. (1972)	300-3000		$1.3x10^{-31}$-$8x10^{-30}$ $cm^6molecule^{-2}s^{-1}$	
Day, et al. (1973)	1000		$1.3x10^{-32}cm^6molecule^{-2}s^{-1}$	10

Comments and Recommendations

There are no definitive measurements on the rate of this process. Numbers given in the literature are rough estimates. We suggest using $k(O + H + M) = 1.3x10^{-29}T^{-1}cm^6molecule^{-2}s^{-1}$. Baulch et al. have summarized other estimates. They range from 10^{-33} to $10^{-30}cm^6molecule^{-2}s^{-1}$. The uncertainty is a factor of 10. This reaction is not very important under combustion conditions.

(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Day, M. J., Thompson, K., and Dixon-Lewis, G., "Some Reactions of Hydroperoxyl and Hydroxyl Radicals at High Temperatures," Symp. Combust. 14, (Combustion Institute, Pittsburgh, 1973) 47

5,5 $O + O + M \rightarrow O_2 + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Hampson (1980) review	200-4000		$5.2\times10^{-35}\exp(900/T)$ (M=Ar) $cm^6 molecule^{-2} s^{-1}$	1.3
	2000-10000		$1.7\times10^{-32}T^{-1/2}$ (M=N_2) $cm^6 molecule^{-2} s^{-1}$	
			$2.2\times10^{-28}T^{-3/2}$ (M=O_2) $cm^6 molecule^{-2} s^{-1}$	

Comments and Recommendations

This is a widely studied system and the data have been extensively reviewed. Details are given in the evaluation of Baulch et al. (1976). We recommend the use of the rate expression for the appropriate collision partner.

(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reaction of the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-Containing Species," (Butterworths, London, 1976)

Hampson, R. F., "Chemical Kinetic and Photochemical Data Sheets for Atmospheric Reactions," Rept. No. FAA-EE-80-17, U. S. Dept. of Transportation, FAA, Washington, D.C. 20234

6,1 $OH + M \rightarrow O + H + M$

$$\log K_p = 5.8041 - 23201.8/T + 231064.2/T^2 - 1.82927\times10^7/T^3$$

Comments and Recommendations

There are no direct measurements. Consistency with the reverse process $O + H + M \rightarrow OH + M$, whose rate is also an estimate, yields through the equilibrium constant:

$$k(OH + M) = 4\times10^{-9}\exp(-50000/T)$$

Uncertainty is a factor of 10.

(R. F. Hampson, May 1983)

6,2 $OH + H_2 \rightarrow H + H_2O$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Cohen, Westberg (1983) review	240-2400		$1.06x10^{-17}T^2exp(-1490/T)$	1.4 to 3
CODATA (1984) evaln.	200-450		$7.7x10^{-12}exp(-2100/T)$	1.3

Comments and Recommendations

Cohen and Westberg's comprehensive survey covers 15 measurements over a wide temperature range and should be used. The CODATA (1984) evaluation for the lower temperature range (200-450 K) is in good agreement.

(W. Tsang, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

6,3 $OH + O_2 \rightarrow O + HO_2$

$\log K_p = 0.0976 - 11622.6/T + 28230.4/T^2$

Comments and Recommendations

Using the rate of the reverse process (7,5) $k(O + HO_2) = 2.9x10^{-11}exp(200/T)cm^3molecule^{-1}s^{-1}$, and the equilibrium constant, we derive

$$k = 3.7x10^{-11}exp(-26500/T)cm^3molecule^{-1}s^{-1}$$

The uncertainty is a factor of 3.

(W. Tsang, May 1983)

6,4 $OH + H \rightarrow O + H_2$ (a)
$OH + H + M \rightarrow H_2O + M$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Cohen, Westberg (1983) review	300-2500		$k_a = 8.1\times10^{-21} T^{2.8} \exp(-1950/T)$	2
Zellner, et al. (1977)	230-300		$k_b(He) = 4.3\times10^{-25} (T^{-2.6})$ $cm^6 molecule^{-2} s^{-1}$ $k_b(Ar) = 1.5\ k_b(He)$ $cm^6 molecule^{-2} s^{-1}$ $k_b(N_2) = 3.2\ k_b(He)$ $cm^6 molecule^{-2} s^{-1}$	1.4
Baulch, et al. (1972)	1000-3000		$k_b(N_2) = 6.1\times10^{-26} (T^{-2})$ $cm^6 molecule^{-2} s^{-1}$ Relative M-efficiencies: $N_2(1.0)$, $Ar(0.38)$, $H_2O(6.3)$	2

Comments and Recommendations

There has been no direct measurement of k_a. The expression recommended by Cohen and Westberg is based on an extensive review of the reverse process. The determination of k_b by Zellner et al. is in reasonable agreement with the recommendation of Baulch et al., and it would appear that the recommended expression given by Baulch et al. is valid over the entire temperature range.

(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

Zellner, R., Erler, K., and Field, D., "Kinetics of the Recombination Reaction $OH + H + M \rightarrow H_2O + M$ at Low Temperature," Symp. Combust. 16, (Combustion Institute, Pittsburgh, 1977) 939

6,5 $OH + O \rightarrow H + O_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Cohen, Westberg (1983) review	200-2500		$7.5x10^{-10}T^{-0.5}exp(-30/T)$	1.4
CODATA (1984) evaln.	220-500		$2.3x10^{-11}exp(+110/T)$	1.2

Comments and Recommendations

Cohen and Westberg's analysis involves low temperature direct measurements and rates of the reverse process at higher temperature and is accepted. The CODATA (1984) evaluation is based on two more recent studies and is in essential agreement with the earlier assessment. (W. Tsang, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

6,6 $OH + OH \rightarrow H_2O + O$ (a)
$OH + OH + M \rightarrow H_2O_2 + M$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Cohen, Westberg (1983) review	300-2000		$k_a=3.5x10^{-16}T^{1.4}exp(200/T)$	2
NASA (1985) evaln.	200-300		$k_a=4.2x10^{-12}exp(-240/T)$ $k_b=6.9x10^{-31}(300/T)^{-0.8}$ $cm^6molecule^{-2}s^{-1}$ ($M=N_2$)	
Wagner, Zellner (1981)	250-580		$k_a=3.2x10^{-12}exp(-240/T)$	
	250-2000		$k_a=exp(-27.73+1.49x10^{-3}T)$ (expression recommended by authors over this temp. range)	

Comments and Recommendations

The expression of Cohen and Westberg for k_a represents a best fit of room temperature and shock tube data in the 1000-2000 K range. It is in substantial agreement with the NASA evaluation and the work of Wagner and Zellner. The rate of reaction (b) is derivable from rates of the reverse reaction (8,1). In the strong collision limit, $k_bo = 2.9x10^{-25}(1/T)^{2.13}cm^6molecule^{-2}s^{-1}$ with an uncertainty of a factor of 2. Collision efficiency as a function of temperature and step size can be found in Table B. For N_2 a step size for deactivation of 800 cm^{-1} leads to $k_b(N_2$, 1 atm) = $1.6x10^{-23}T^{-3}cm^6molecule^{-2}s^{-1}$(500-2500 K). It is near the low pressure limit and also applicable up to 10 atm. However, the temperature dependence is different than that measured between 200-300 K. From the reverse process, step size for deactivation with argon is ~600 cm^{-1} leading to a rate of about a factor of 1.6 slower than that for N_2. H_2O is strong collider. For other polyatomics we suggest using step sizes in the 1000-2000 cm^{-1} range. Small pressure corrections can be found in Table A. The uncertainty is a factor of 2.

Table A. Values of $\log(k/k_bo)$: dependence on concentration and temperature.

log[M]/	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
17.0	-0.05	-0.03	-0.02	-0.02	-0.01							
18.0	-0.17	-0.10	-0.06	-0.05	-0.05	-0.04	-0.03	-0.03	-0.03	-0.02	-0.01	-0.01
19.0	-0.43	-0.28	-0.17	-0.14	-0.14	-0.12	-0.10	-0.08	-0.08	-0.07	-0.06	-0.05
20.0	-0.87	-0.69	-0.55	-0.44	-0.38	-0.33	-0.28	-0.26	-0.27	-0.21	-0.19	-0.17
21.0	-1.81	-1.43	-1.03	-0.91	-0.91	-0.81	-0.73	-0.66	-0.61	-0.55	-0.50	-0.47

Table B. Collision efficiency β_c as a function of downward step size and temperature for process b.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.32	0.52	0.70	0.83
500	0.077	0.19	0.37	0.57	0.74
700	0.044	0.12	0.27	0.46	0.66
900	0.028	0.082	0.20	0.38	0.58
1100	0.018	0.058	0.15	0.31	0.52
1300	0.013	0.042	0.12	0.26	0.46
1500	$9.5x10^{-3}$	0.032	0.091	0.22	0.40
1700	$7.1x10^{-3}$	0.024	0.072	0.18	0.35
1900	$5.3x10^{-3}$	0.019	0.058	0.15	0.31
2100	$4.1x10^{-3}$	0.015	0.046	0.13	0.27
2300	$3.2x10^{-3}$	0.015	0.038	0.10	0.24
2500	$2.5x10^{-3}$	0.009	0.031	0.089	0.21

(W. Tsang, October 1984)

References

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

NASA(1985). Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation No. 7, NASA Panel for Data Evaluation, JPL Publication 85-37 July 1985

Wagner, G., and Zellner, R., "Temperature Dependence of the Reaction OH + OH → H_2O + O," Ber. Bunsenges. Phys. Chem. 85, 1122 (1981)

7,1 $HO_2 + M \rightarrow H + O_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = 5.6741 - 11494.3/T + 147979/T^2$				
Baulch, et al. (1972)	300-2000		$3.5 \times 10^{-9}\exp(-23000/T)$ (M=Ar)	

Comments and Recommendations

There are no direct experimental measurements on this system. From the equilibrium constant and the reverse reaction, we obtain:

$k_o = 2\times10^{-5}T^{-1.18}\exp(-24363/T)cm^3molecule^{-1}s^{-1}$ 300-2000 K ($M=N_2$)

$k_o = 6.3\times10^{-7}T^{-.76}\exp(-24350/T)cm^3molecule^{-1}s^{-1}$ 300-2000 K (M=Ar)

The uncertainty is a factor of 3.

The expression for Ar given here is different from that of Baulch, et al., due to new reverse rates and thermochemistry. It is based on the evaluation of the reverse process by Slack (Combust. Flame 28, 241 (1977)). Collisional efficiencies at room temperature from the reverse process on a pressure basis are Ar(1), N_2(2.8), He(1), H_2(3.0), CH_4(21). The value for CH_4 seems extremely high. The uncertainty is a factor of 3.
(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

7,2 $HO_2 + H_2 \rightarrow H_2O_2 + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = -0.2071 - 4071.5/T + 103193.6/T^2 - 0.94947\times10^7/T^3$				
Baldwin, Walker (1979)	773		2.7×10^{-18}	
Hampson (1980) review	300-800		$1.2\times10^{-12}\exp(-9400/T)$	

Comments and Recommendations

The Arrhenius expression given above was obtained on the basis of the measurements of Baldwin and Walker and values calculated from the rate constants of the reverse process. $H + H_2O_2 \rightarrow H_2 + HO_2$ (8,4a). These measurements (8,4) may be subject to some ambiguity. We suggest the use of $k(HO_2 + H_2 \rightarrow H_2O_2 + H) = 5\times10^{-11}\exp(-13100/T)cm^3molecule^{-1}s^{-1}$ in order

to take into account new thermochemistry for HO_2. The uncertainty is a factor of 3.
(W. Tsang, May 1983)

References

Baldwin, R. R., and Walker, R., "Rate Constants for Hydrogen + Oxygen System, and for H Atoms and OH Radicals + Alkanes," J. Chem. Soc., Faraday Trans. I 75, 140 (1979)

Hampson, R. F., "Chemical Kinetic and Photochemical Data Sheets for Atmospheric Reactions," Rept. No. FAA-EE-80-17, U.S. Dept. of Transportation, FAA, Washington, D.C.

7,4 $HO_2 + H \rightarrow 2OH$ (a)
$\rightarrow H_2 + O_2$ (b)
$\rightarrow H_2O + O$ (c)

	Conditions			
Reference	Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
CODATA (1984) evaln.	298		k_a=6.4x10^{-11}	1.5
			k_b=6.7x10^{-12}	2
			k_c=3.0x10^{-12}	3
Baldwin, et al. (1974)	773		$k_{a+c} \simeq 1.6x10^{-10}$	
			k_b=2.8x10^{-11}	2
			determined from $k_{a+c}/k(H + O_2 \rightarrow HO + O)$ x $k^{1/2}(2HO_2 \rightarrow H_2O_2 + O_2)$ and $k_b/k(H + O_2 \rightarrow HO + H)$ x $k^{1/2}(2HO_2 \rightarrow H_2O_2 + O_2)$	

Comments and Recommendations

Combination of the high temperature data of Baldwin et al. assuming k_a>>k_c and the room temperature results of Sridharan et al. yields $k_a = 2.8x10^{-10}exp(-440/T)$ and $k_b = 1.1x10^{-10}exp(-1070/T)cm^3molecule^{-1}s^{-1}$ over the temperature range 298-773 K. The recent room temperature results of Sridharan et al. which provide the basis for the CODATA recommendation are preferred over earlier room temperature data. The uncertainty is a factor of 2.
(R. F. Hampson, October 1983)

References

Baldwin, R. R., Fuller, M. E., Hillman, J. S., Jackson, D., and Walker, R. W., "Second Limit of Hydrogen + Oxygen Mixtures: The Reaction H + HO_2," J. Chem. Soc., Faraday Trans. I 70, 635 (1974)

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Sridharan, U. C., Qiu, L. S., and Kaufman, F., "Kinetics and Product Channels of the Reactions of HO_2 with O and H Atoms at 296 K," J. Phys. Chem. 86, 4569 (1982)

7,5 $HO_2 + O \rightarrow OH + O_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
CODATA (1984)	200-400		$2.9\times10^{-11}\exp(+200/T)$	1.25
	298		5.7×10^{-11}	

Comments and Recommendations

The CODATA values are based on results of four recent direct studies which are in good agreement.

(W. Tsang, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

7,6 $HO_2 + OH \rightarrow H_2O + O_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Troe (1968)	1400 Shock tube decomposition of H_2O_2		1.6×10^{-11}	2
CODATA (1984) evaln.	298		$(6.6+4.4\times P(atm))\times10^{-11}$	1.6

Comments and Recommendations

The room temperature value of this rate constant is near the collisional rate and is reasonably well established. The higher temperature results are somewhat less certain. There is the possibility of a small negative temperature dependence and the expression $2.4\times10^{-8}T^{-1}cm^3molecule^{-1}s^{-1}$ is suggested. The uncertainty is a factor of 2.

(W. Tsang, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Troe, J., "Ultraviolettspektrum und Reaktionen des HO_2-Radicals im Thermischen Zerfall von H_2O_2," Ber. Bunsenges. Physik. Chem. 73, 946 (1979)

7,7 $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Walker (1975) review	300-1200		$3.3x10^{-12}$	
CODATA (1984) evaln.	230-420		$2.2x10^{-13}exp(600/T) + 1.9x10^{-33}[N_2]exp(980/T)$	
	298		$1.5x10^{-12} + 5.4x10^{-32}[N_2]$	

Comments and Recommendations

There is some evidence of temperature and pressure dependence for this reaction near room temperatures. We suggest using $3x10^{-12}cm^3molecule^{-1}s^{-1}$ at all temperatures with an uncertainty of a factor of 3 for temperatures in excess of 500 K.

(W. Tsang, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Walker, R. W., "A Critical Survey of Rate Constants for Reaction in Gas-Phase Hydrocarbon Oxidation," in "Reaction Kinetics," A Specialist Report (The Chemical Society, Burlington House, London, 1975) Vol. 1, pg. 161

8,1 $H_2O_2 + M \rightarrow 2OH + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$log K_p = 7.363 - 11385.8/T + 138674/T^2$				
Baulch, et al. (1972) review	700-1500		$2x10^{-7}exp(-22900/T)$ ($M=N_2$) Relative M-efficiencies: Ar(0.7), O_2(~0.7), H_2O(~6)	

Comments and Recommendations

The recommended expression given by Baulch, et al. is derived from a comprehensive review of experimental results. RRKM calculations are in very good agreement with experimental data in both forward and reverse directions (see data sheet for reverse reaction). The bimolecular rate expression (strong collision limit) is $k_o=10^{3.77}(1/T)^{2.87}exp(-25899/T)$ $cm^3molecule^{-1}s^{-1}$. The small pressure dependence and the dependence of collision efficiency on temperature and step-size down can be found in Tables A and B. The recommended rate expression is: $k(N_2, 1 atm) = 10^{9.33}(1/T)^{4.86}exp(-26795/T)cm^3molecule^{-1}s^{-1}$ (T>500 K) with step size for deactivation for N_2 of 800 cm^{-1}. This is essentially the limiting low pressure expression and is also applicable up to 10 atm. Step size for argon should be ~600 cm^{-1}. H_2O is a strong collider. We suggest the use of step sizes of 1000-2000 cm^{-1} for other polyatomics. The estimated uncertainty is a factor of 2.

Table A. Values of $\log(k/k_o)$: dependence on concentration and temperature.

log[M]/	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
17.0	-0.05	-0.03	-0.02	-0.02	-0.01							
18.0	-0.17	-0.10	-0.07	-0.06	-0.05	-0.04	-0.03	-0.03	-0.02	-0.02	-0.01	-0.01
19.0	-0.43	-0.28	-0.20	-0.17	-0.14	-0.12	-0.10	-0.08	-0.07	-0.07	-0.06	-0.05
20.0	-0.87	-0.69	-0.55	-0.44	-0.38	-0.33	-0.28	-0.23	-0.21	-0. 21	-0.19	-0.07
21.0	-1.81	-1.43	-1.10	-1.03	-0.91	-0.81	-0.66	-0.61	-0.55	-0.50	-0.50	-0.47

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.32	0.52	0.70	0.83
500	0.077	0.19	0.37	0.57	0.74
700	0.044	0.12	0.27	0.46	0.66
900	0.028	0.082	0.20	0.38	0.58
1100	0.018	0.058	0.15	0.31	0.52
1300	0.013	0.042	0.12	0.26	0.46
1500	$9.5x10^{-3}$	0.032	0.091	0.22	0.40
1700	$7.1x10^{-3}$	0.024	0.072	0.18	0.35
1900	$5.3x10^{-3}$	0.019	0.058	0.15	0.31
2100	$4.1x10^{-3}$	0.015	0.046	0.13	0.27
2300	$3.2x10^{-3}$	0.015	0.038	0.10	0.24
2500	$2.5x10^{-3}$	0.009	0.031	0.089	0.21

(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

8,3 $H_2O_2 + O_2 \rightarrow 2HO_2$

$\log K_p = 0.624 - 8000.6/T - 36256/T^2$

Comments and Recommendations

There are no direct measurements on the rate of this process. From the

rate of the reverse reaction and the thermodynamics we obtain k($H_2O_2 + O_2 \rightarrow 2HO_2$)= 9×10^{-11}exp(-20000/T)$cm^3molecule^{-1}s^{-1}$. The estimated uncertainty is a factor of 5.
(W. Tsang, May 1983)

8,4 $H_2O_2 + H \rightarrow H_2 + HO_2$ (a)
$\rightarrow H_2O + OH$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Baldwin, Walker (1979)	773		$k_a=4.3\times10^{-13}$ $k_b=3.6\times10^{-12}$	2
Klemm, et al. (1975)	283-353		$k_{a+b} = 5\times10^{-12}$exp(-1400/T)	1.2
Baulch, et al. (1972)	300-800		$k_a=2.8\times10^{-12}$exp(-1900/T)	

Comments and Recommendations

The relative importance of the two channels at low temperature is still uncertain. The total rate determined via flash photolysis - resonance fluorescence by Klemm et al. is undoubtedly correct, and accepting their suggestion that this is for the most part k_b, then combination of high and low temperature results yields $k_b \approx 4\times10^{-11}$exp(-2000/T)$cm^3molecule^{-1}s^{-1}$ With Baldwin and Walker's k_a as a base we estimate $k_a \sim 8\times10^{-11}$exp(-4000/T)$cm^3molecule^{-1}s^{-1}$. The estimated uncertainties for k_a and k_b are 25% at room temperature, a factor of 2 at 773 K, and a factor of 5 at temperatures above 1000 K. The expression recommended by Baulch et al. is compatible with the high temperature results but is dependent on low temperature measurements that are now superseded by that of Klemm et al.
(W. Tsang, May 1983)

References

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Klemm, R. B., Payne, W. A., and Stief, L. J., "Absolute Rate Parameters for the Reaction of Atomic Hydrogen with H_2O_2," Int. J. Chem. Kinet., Symp. No. 1, 61 (1975)

8,5 $H_2O_2 + O \rightarrow OH + HO_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
CODATA (1984) evaln.	250-390		1.4×10^{-12}exp(-2000/T)	2
	298		1.7×10^{-15}	
Albers, et al. (1969)	300-800		4.7×10^{-11}exp(-3200/T)	upper limit

Comments and Recommendations

The CODATA recommendation is undoubtedly valid at low temperatures. For higher temperature (>500 K) applications we suggest the use of the expression $k = 1.6\times10^{-17}T^2\exp(-2000/T)\mathrm{cm^3 molecule^{-1}s^{-1}}$ with an uncertainty of a factor of 3.

(W. Tsang, October 1984)

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8,6 $H_2O_2 + OH \rightarrow H_2O + HO_2$

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/\mathrm{cm^3 molecule^{-1}s^{-1}}$	Uncertainty factor
CODATA (1984) evaln.	240-460		$2.9\times10^{-12}\exp(-160/T)$	1.25
	298		1.7×10^{-12}	
NASA (1985) evaln.	200-300		$3.1\times10^{-12}\exp(-187/T)$	
	298		1.7×10^{-12}	
Baulch, et al. (1972) evaln.	300-800		$1.7\times10^{-11}\exp(-910/T)$	1.50

Comments and Recommendations

The lower temperature results are in excellent accord. We suggest use of the expression recommended in the CODATA evaluation except that at temperatures in excess of 1000 K the uncertainty is probably a factor of 3.

(W. Tsang, July 1985)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

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Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

9,1 $H_2O + M \rightarrow H + OH + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Baulch, et al. (1972) review	2000-6000		$5.8x10^{-9}exp(-52900/T)$ ($M=N_2$) Relative M-efficiencies: $N_2(1.0)$, $Ar(0.4)$, $H_2O(6.2)$	1.5

Comments and Recommendations

The expression given above is based on a review of direct determinations combined with an analysis of the reverse process and the equilibrium constant. In view of the good agreement between recent determinations of the reverse rate near room temperature and the recommendations of Baulch et al. based on higher temperature measurements, this rate expression is probably applicable over all relevant temperature ranges.
(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

9,4 $H_2O + H \rightarrow H_2 + OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Cohen, Westberg (1983) review	400-2400		$1.03x10^{-16}T^{1.9}exp(-9265/T)$	2 to 3

Comments and Recommendations

This expression is derived from the reverse rate and equilibrium constant.
(W. Tsang, May 1983)

References

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

9,5 $H_2O + O \rightarrow 2OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Cohen, Westberg (1983) review	400-2000		$7.6 \times 10^{-15} T^{1.3} \exp(-8605/T)$	2.5

Comments and Recommendations

This expression is based on a review of experimental data and transition state calculations for the reverse rate combined with the equilibrium constant.

(W. Tsang, May 1983)

References

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

10,1 $CH_4 + M \rightarrow CH_3 + H + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
$\log K_p = 7.627 - 23720/T + 134770/T^2$				
Tabayashi, Bauer (1979)	1950-2770	$(14\text{-}50) \times 10^{17}$ 10-20% CH_4 in Ar	$1.67 \times 10^{-7} \exp(-43200/T)$	2
Heffington, et al. (1977)	2000-2700	$(6\text{-}17) \times 10^{18}$ 1-10% CH_4 in Ar	$3.7 \times 10^{-7} \exp(-45400/T)$	3
Chen, et al. (1975)	995	$(5\text{-}70) \times 10^{17}$ (CH_4)	$(0.74\text{-}2.82) \times 10^{-8}\ s^{-1}$	1.25
	1038	$(3\text{-}70) \times 10^{17}$ (CH_4)	$(0.39\text{-}2.57) \times 10^{-7}\ s^{-1}$	
	1068	$(25\text{-}70) \times 10^{17}$ (CH_4)	$(0.98\text{-}8.71) \times 10^{-7}\ s^{-1}$	
	1103	$(5\text{-}65) \times 10^{17}$ (CH_4)	$(0.69\text{-}3.86) \times 10^{-6}\ s^{-1}$	
Gardiner, et al. (1975)	2000-2700	$(6\text{-}10) \times 10^{17}$, 0.4-10% CH_4 in rare gases and H_2	$3.8 \times 10^{-10} \exp(-32500/T)$	large
Roth, Just (1975)	1700-2300	6×10^{18} 5-200 ppm CH_4	$7.9 \times 10^{-7} \exp(-46900/T)$	2
Vompe (1973)	2000-2700	2×10^{18} 2-5% CH_4 in N_2	$4 \times 10^{9} \exp(-31700/T) s^{-1}$	large
Napier, Subrahmanyam (1972)	1750-2700	4×10^{19} 10% CH_4 in Ar	$3.8 \times 10^{13} \exp(-47100/T) s^{-1}$	large
Hartig, et al. (1971)	1850-2500	1×10^{21}	$2 \times 10^{14} \exp(-50900/T) s^{-1}$	3
		3×10^{19}	$1.3 \times 10^{13} \exp(-48300/T) s^{-1}$	
Benson, O'Neal (1970) review			$k_f^{\infty} \simeq 2 \times 10^{15} \exp(-52400/T) s^{-1}$	

Comments and Recommendations

All of the more recent work subsequent to Benson and O'Neal's review, except for that of Chen et al., are shock tube experiments. Within the limitations of the methodology the results are in good agreement. In the cases where the rate parameters are completely unacceptable, we have made comparisons at the midpoint of the temperature range covered. All of these studies, except that of Hartig and coworkers, are deep in the fall-off region; thus they permit a determination of the third body efficiencies. In the analysis of the data, we begin with the measurements of Chen et al. and the reverse rate determined by Cheng et al. These are close to the high pressure limit. This suggests that the higher pressure results of Hartig et al. are a factor of 3 too low. On this basis the high pressure rate constant from 500-2700 K can be written as:

$$k_\infty = 10^{15.57}\exp(-52246/T)\,s^{-1}$$

with an uncertainty of 50% up to 1500 K and a factor of 3 at higher temperatures. In the presence of methane or ethane a step size for deactivation of 2000 cm^{-1} fits the experimental results at 300 and 1000 K. The correction factors for 0.1, 1 and 10 atms are:

$$\log(k(CH_4,\ 0.1)/k_\infty) = 0.174 - 1.104\times10^{-3}T + 1.82\times10^{-8}T^2$$
$$\log(k(CH_4,\ 1)/k_\infty) = 0.155 - 4.391\times10^{-4}T - 1.119\times10^{-7}T^2$$
$$\log(k(CH_4,\ 10)/k_\infty) = 0.021 + 2.031\times10^{-5}T - 1.61\times10^{-7}T^2$$

For argon as the deactivator a step size down of 600 cm^{-1} fits the data from 1200 to 2500 K. The correction factors at 0.1, 1 and 10 atms are:

$$\log(k(Ar,\ 0.1)/k_\infty) = 0.225 - 1.652\times10^{-3}T + 1.038\times10^{-7}T^2$$
$$\log(k(Ar,\ 1)/k_\infty) = 0.275 - 8.745\times10^{-4}T - 7.107\times10^{-8}T^2$$
$$\log(k(Ar,\ 10)/k_\infty) = 0.107 - 1.743\times10^{-4}T - 1.9270\times10^{-7}T^2$$

In the temperature range 300-700 K step size for deactivation for rare gases and H_2 appears to be of the order of 100-200 cm^{-1}. This is based on the reverse reaction. Table A contains data on fall-off behavior for strong colliders. Collision efficiencies as a function of step size and temperature can be found in Table B.

Table A. Values of $\log(k/k_\infty)$: dependence on concentration and temperature.

log[M]/	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.66	-1.81	-1.96	-2.11	-2.26	-2.40	-2.55	-2.68	-2.81	-2.93	-3.05	-3.16
16.5	-1.23	-1.37	-1.51	-1.66	-1.80	-1.94	-2.09	-2.21	-2.35	-2.47	-2.58	-2.69
17.0	-0.84	-0.97	-1.1	-1.24	-1.38	-1.51	-1.65	-1.78	-1.91	-2.02	-2.13	-2.26
17.5	-0.52	-0.63	-0.75	-0.88	-1.01	-1.13	-1.26	-1.38	-1.50	-1.61	-1.71	-1.81
18.0	-0.28	-0.37	-0.47	-0.58	-0.69	-0.80	-0.92	-1.03	-1.14	-1.24	-1.33	-1.42
18.5	-0.13	-0.19	-0.27	-0.35	-0.44	-0.53	-0.63	-0.73	-0.82	-0.99	-0.99	-1.07
19.0	-0.05	-0.09	-0.14	-0.19	-0.26	-0.33	-0.41	-0.48	-0.56	-0.63	-0.70	-0.77
19.5	-0.02	-0.04	-0.06	-0.09	-0.14	-0.18	-0.24	-0.29	-0.35	-0.41	-0.46	-0.51
20.0	-0.01	-0.01	-0.02	-0.04	-0.06	-0.09	-0.12	-0.16	-0.20	-0.24	-0.27	-0.31
20.5			-0.01	-0.02	-0.02	-0.04	-0.06	-0.08	-0.10	-0.12	-0.14	-0.17
21.0				-0.01	-0.01	-0.01	-0.02	-0.03	-0.04	-0.05	-0.06	-0.08

Table B. Collision efficiency β_c as a function of downward step size and temperature

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.32	0.53	0.71	0.83
500	0.08	0.19	0.37	0.58	0.74
700	0.05	0.13	0.27	0.47	0.66
900	0.03	0.09	0.21	0.39	0.59
1100	0.02	0.06	0.16	0.33	0.53
1300	0.015	0.046	0.13	0.27	0.47
1500	0.011	0.035	0.11	0.23	0.42
1700	0.009	0.029	0.085	0.20	0.39
1900	0.006	0.021	0.065	0.17	0.33
2100	0.005	0.017	0.053	0.14	0.30
2300	0.004	0.014	0.044	0.12	0.27
2500	0.003	0.011	0.037	0.10	0.24

(W. Tsang, October 1983)

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Tabayashi, K., and Bauer, S. H., "The Early Stages of Pyrolysis and Oxidation of Methane," Combust. Flame 34, 63 (1979)

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10,3 $CH_4 + O_2 \rightarrow CH_3 + HO_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Walker (1974) review			$6.7 \times 10^{-11} \exp(-28640/T)$	5

Comments and Recommendations

There are no direct measurements of the rate of this reaction. The estimate given in Walker's review is based on the rates of related processes: O_2 + HCHO, H + HO_2, HO_2 + HO_2, etc.
(W. Tsang, May 1983)

References

Walker, R. W., "A Critical Survey of Rate Constants for Reactions in Gas-Phase Hydrocarbon Oxidation," in "Reaction Kinetics," A Specialist Report (The Chemical Society, Burlington House, London, 1975) Vol. 1, pg 161

10,4 $CH_4 + H \rightarrow CH_3 + H_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Sepehrad, et al.	640-818	0.6-2.2x10^{17} Ar	$3 \times 10^{-10} \exp(-6631/T)$	1.5
(1979) review			$1.3 \times 10^{-10} \exp(-6005/T)$	
Shaw (1978) review			$2.34 \times 10^{-17} T^2 \exp(-4449/T)$	
Clark, Dove (1973) review			$3.73 \times 10^{-20} T^3 \exp(-4406/T)$	
Walker (1969) review			$2.1 \times 10^{-10} \exp(-5992/T)$	

Comments and Recommendations

The literature on this reaction is extensive. The controversial issue is the degree of curvature of the Arrhenius plot. Since an absolute Arrhenius dependence over the 300-2500 K temperature range cannot be justified on the basis of any known theory, we believe that a temperature dependent A-factor is to be expected. We have carried out BEBO calculations and confirmed the results of Clark and Dove. We favor this rate expression because of the better fit at higher temperatures. The estimated uncertainty is ±30% in the 500-800 K range and a factor of 3 at 2500 K.
(W. Tsang, May 1983)

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Walker, R. W., "Activation Energies of the Reversible Reaction between Hydrogen Atoms and Methane to give Hydrogen and Methyl Radicals" J. Chem. Soc., 2391 (1968)

10,5 $CH_4 + O \rightarrow CH_3 + OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Herron, Huie (1973) evaln.	350-1000		$3.5x10^{-11}exp(-4550/T)$	1.3
Barassin, Combourieu (1974)	354-443	$7x10^{16}$ He	$5.8x10^{-11}exp(-4530/T)$	
Brabbs, Brokaw (1975)	1300-2000	$5x10^{18}$ Ar	$3.2x10^{-10}exp(-5900/T)$	
Roth, Just (1977)	1500-2250	$7x10^{18}$ Ar	$6.8x10^{-10}exp(-7030/T)$	
	300-2250		$1.94x10^{-17}T^{2.08}exp(-3840/T)$ (recn. including low T data)	
Shaw (1978) extrapoln.	300-2000		$8.5x10^{-18}T^2exp(-3240/T)$	
Felder, Fontijn (1979, 1980)	420-1670	$(0.2-90)x10^{17}$ N_2	$2.63x10^{-18}T^{2.36}exp(-3730/T)$	
Klemm, et al. (1981)	474-1156	$(0.2-40)x10^{17}$ Ar	$2.0x10^{-10}exp(-5435/T)$	
	475-2250		$5.24x10^{-12}T^{0.5}exp(-5180/T)$ (recn. including high T data)	

Comments and Recommendations

The most reliable rate data for the combustion chemistry temperature range are those from the recent studies by Roth and Just (1977), Felder and Fontijn (1980) and Klemm et al. (1981). Based on these data, we recommend the expression $k(CH_4 + O \rightarrow CH_3 + OH) - 1.7x10^{-15}T^{1.5}exp(-4330/T)$ $cm^3molecule^{-1}s^{-1}$ with an uncertainty of ±25%. These studies are all in good agreement, and this rate constant is well known over an extremely wide temperature range.

(R. F. Hampson, May 1983)

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Shaw, R., "Semi-Empirical Extrapolation and Estimation of Rate Constants for Abstraction of H from Methane by H, O, HO, and O_2," J. Phys. Chem. Ref. Data 7, 1179 (1978)

10,6 $CH_4 + OH \rightarrow CH_3 + H_2O$

Reference	Conditions Temp./K	Conditions [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = 2.60 - 0.5 \log T + 2788/T$				
Cohen, Westberg (1983) evaln.	240-2000		$3.2\times10^{-19}T^{2.4}\exp(-1060/T)$	1.25 T=240-500 K incr. to 1.6 at 2000 K
Jeong, Kaufman (1982)	269-473	1×10^{17}	$6.27\times10^{-18}T^{2.0}\exp(-1263/T)$	

Comments and Recommendations

This evaluation accepts the recommendation given in the Cohen and Westberg (1983) evaluation. The only data not considered by Cohen and Westberg are the recent data of Jeong and Kaufman (1982) which are in good agreement with that recommendation. The recommendation is based on the data of Tully and Ravishankara (1980) from 300-1000 K and that of Zellner and Steinert (1976) from 300-900 K with the former being favored, and the results of their own transition state theory calculation above 1000 K. The results of a TST calculation by Ernst, Wagner and Zellner (1978) gives essentially the same numerical results. Earlier work was reviewed by Shaw (1978).

(R. F. Hampson, May 1983)

References

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10,7 $CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$

Comments and Recommendations

There have been no measurements on this process. We estimate $k(CH_4 + HO_2 \rightarrow CH_3 + H_2O_2) = 3x10^{-13}exp(-9350/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of factor of 5. It is based on the relation given by Walker for HO_2 attack on alkanes. (W. Tsang, May 1983)

References

Walker, R. W., "Rate Constants for Reaction in Gas-Phase Hydrocarbon Oxidation", Chapter 7 in "Gas Kinetics and Energy Transfer," A Specialist Periodical Report (The Chemical Society, London, 1977) Vol. 2, pg. 296

11,1 $C_2H_6 \rightarrow 2CH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
log K_p = 8.97 - 20017/T + 50209/T^2				
Olson, et al. (1979)	1300-2500	$7\text{-}27x10^{17}$ Ar	$10^{-5.79}exp(-35360/T)$	3
Baulch, Duxbury (1980) review	750-1500		$2.4x10^{16}exp((-44010\pm3170)/T)/s$	1.5
Burcat, et al. (1973)	1200-1430	$9\text{-}33x10^{18}$	$k\infty=7.9x10^{16}exp(-45060/T)s^{-1}$	3
Trenwith (1967)	873	$3\text{-}30x10^{16}$	$k/k(M=C_2H_6)$ (collision basis) Relative M efficiences: $C_2H_6(1.0)$, $N_2(.25)$, $CO_2(.33)$, He(.17), Ne(.18), Ar(.26), Kr(.31), $H_2O(.88)$	2
Chiang, Skinner (1981)	1240-1500	$1.4x10^{19}$ Ar	$2.8x10^{15}exp(-42417/T)/s$	2

Comments and Recommendations

This is an extensively studied reaction. Data have been fit from room temperature up to 1400 K on the basis of RRKM calculations using the restricted rotor model. The rate expression at high pressures can best be represented by the expression $k\infty = 10^{22.5}(T^{-1.79})\exp(-45834/T)s^{-1}$ with an uncertainty of ±50%. The pressure dependence on a strong collision basis can be found in the accompanying Table A.

For weak colliders the rate of the reverse process at 300, 577 and 1350 K in the presence of argon (see 16.16) leads to downward step sizes of 300 cm^{-1} at the lower two temperatures and 600 cm^{-1} at the higher temperature. On this basis we suggest $k/k\infty$ values [with a 600 wave number step size down] for argon and nitrogen of the following form:

$$\log(k(Ar, .1)/k\infty) = -0.155 + 9.716x10^{-4}T - 1.533x10^{-6}T^2 + 2.614x10^{-10}T^3$$
$$\log(k(Ar, 1)/k\infty) = -0.235 + 1.033x10^{-3}T - 1.114x10^{-6}T^2 + 1.425x10^{-10}T^3$$
$$\log(k(Ar, 10)/k\infty) = -0.151 + 5.551x10^{-4}T - 4.296x10^{-7}T^2 - 1.081x10^{-11}T^3$$

This should be valid at temperatures in excess of 1000 K.

In the presence of ethane in the temperature range 800-900 K the experimental data indicates a step size down for collisional deactivation of 1000 cm^{-1}. This is in accord with room temperatures results. We suggest the following rate expressions with ethane as a deactivator:

$$\log(k(C_2H_6, 0.1)/k\infty) = -0.185 + 9.743x10^{-4}T - 1.315x10^{-6}T^2 + 2.051x10^{-10}T^3$$
$$\log(k(C_2H_6, 1)/k\infty) = -0.20 + 8.202x10^{-4}T - 7.964x10^{-7}T^2 + 7.452x10^{-11}T^3$$
$$\log(k(C_2H_6, 10)/k\infty) = -0.087 + 2.878x10^{-4}T - 1.587x10^{-7}T^2 - 5.638x10^{-11}T^3$$

It should be noted that the relative collisional efficiency for ethane and argon differ by a factor of 3 from the results of Trenwith (1967). Their results do lead to comparable efficiencies for Ar, N_2 and Kr. H_2O is a strong collider. Table B summarizes collisional efficiencies as a function of step size down and temperature.

Table A. Values of $\log(k/k\infty)$: dependence on concentration and temperature.

log[M]/	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.23	-0.45	-0.71	-0.99	-1.25	-1.52	-1.78	-2.03	-2.28	-2.51	-2.73
16.5	-0.03	-0.12	-0.29	-0.49	-0.72	-0.95	-1.19	-1.42	-1.66	-1.89	-2.10	-2.31
17.0	-0.01	-0.06	-0.17	-0.32	-0.50	-0.69	-0.89	-1.10	-1.31	-1.51	-1.71	-1.90
17.5		-0.03	-0.09	-0.19	-0.32	-0.47	-0.64	-0.81	-0.99	-1.17	-1.35	-1.53
18.0		-0.01	-0.04	-0.10	-0.19	-0.30	-0.42	-0.57	-0.72	-0.87	-1.03	-1.18
18.5			-0.02	-0.05	-0.10	-0.17	-0.26	-0.37	-0.49	-0.61	-0.74	-0.88
19.0			-0.01	-0.02	-0.045	-0.09	-0.15	-0.22	-0.31	-0.40	-0.50	-0.61
19.5				-0.01	-0.02	-0.04	-0.07	-0.12	-0.17	-0.24	-0.31	-0.39
20.0					-0.01	-0.02	-0.03	-0.06	-0.09	-0.13	-0.17	-0.23
20.5						-0.01	-0.01	-0.02	-0.04	-0.06	-0.09	-0.12
21.0								-0.01	-0.015	-0.02	-0.04	-0.05

Table B. Collision efficiency β_c as a function of downward step size and temperature

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
300	0.31	0.46	0.56	0.65	0.80
500	0.18	0.30	0.40	0.50	0.69
700	0.11	0.20	0.29	0.39	0.59
900	0.07	0.14	0.21	0.30	0.50
1100	0.046	0.093	0.15	0.23	0.42
1300	0.031	0.069	0.11	0.17	0.35
1500	0.022	0.050	0.082	0.13	0.29
1700	0.015	0.036	0.061	0.10	0.23
1900	0.011	0.026	0.044	0.076	0.19
2100	0.0074	0.018	0.032	0.057	0.15
2300	0.0051	0.013	0.023	0.042	0.12
2500	0.0036	0.009	0.017	0.031	0.09

(W. Tsang, October 1984)

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Burcat, A., Skinner, G. B., Crossley, R. W., and Scheller, K., "High Temperature Decomposition of Ethane," Int. J. Chem. Kinet. 5, 345 (1973)

Chiang, C. C., and Skinner, G., "Resonance Absorption Measurements of Atom Concentrations in Reacting Gas Mixtures 'Pyrolysis of C_2H_6 and C_2D_6 Behind Shock Waves'," J. Phys. Chem. 85, 3126 (1981)

Olson, D. B., Tanzawa, T., and Gardiner, W. C., Jr., "Thermal Decomposition of Ethane," Int. J. Chem. Kinet. 11, 23 (1979)

Trenwith, A. B., "Dissociation of Ethane: An Energy Transfer Study," Trans. Faraday Soc. 63, 2452 (1967)

11,3 $C_2H_6 + O_2 \rightarrow C_2H_5 + HO_2$

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Walker (1974) review			$6.7x10^{-11}exp(-25600/T)$	5

Comments and Recommendations

There are no measurements of the rate of this reaction. Estimate in Walker's review is based on the related rates for O_2 + HCHO, H + HO_2, HO_2 + HO_2, etc. Uncertainty factor is 5.
(W. Tsang, May 1983)

References

Walker, R. W., "A Critical Survey of Rate Constants for Reactions of Gas-Phase Hydrocarbon Oxidation," in "Reaction Kinetics," A Specialist Report (The Chemical Society, Burlington House, London, 1975) Vol. 1 pg. 161

11,4 $C_2H_6 + H \rightarrow C_2H_5 + H_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1}s^{-1}$	Uncertainty factor
Jones, et al. (1977)	357-544	$8.6x10^{16}$	$1.8x10^{-10}exp(-4640/T)$	1.5
Camilleri, et al. (1974)	503-753	$1.8x10^{17}$	$3.1x10^{-10}exp(-4920/T)$	1.5
Clark, Dove (1973) review	300-1800		$9x10^{-22}T^{3.5}exp(-2600/T)$	
Baldwin, Walker (1979) review			$2.2x10^{-10}exp(-4715/T)$	
Lede, Villermaux (1978)	281-347	$(3-14)x10^{18}$	$8.3x10^{-11}exp(-4580/T)$	2

Comments and Recommendations

The experimental results do not dictate any particular T dependence of the pre-exponential factor. However, since there is no reason to expect a constant A-factor the expression of Clark and Dove is preferred. The uncertainty factor is 1.5 up to 1000 K, increasing to 3 at the highest temperatures. The discharge flow experiments of Camilleri and Jones and the review of Baldwin and Walker are in accord with the rate constants of Clark and Dove over the 400-1100 K range. The results of Lede and Villermaux may be indicative of a lesser curvature. If this is the case the higher temperature rate constants from Clark and Dove will be overestimates.
(W. Tsang, October 1983)

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Jones, D., Morgan, P. A., and Purnell, J. H., "Mass Spectrometric Study of the Reaction of Hydrogen Atoms with Ethane," J. Chem. Soc., Faraday Trans. I 73, 1311 (1977)

Lede, J., and Villermaux, J., "Mesure de la Constante de Vitesse de Rèaction des Atomes d'Hydrogène sur l'Ethane et le Propane en Rèacteurs Tubulaire et Parfaitement Agitè Ouverts," Can. J. Chem. 56, 392 (1978)

11,5 $C_2H_6 + O \rightarrow C_2H_5 + OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1}s^{-1}$	Uncertainty factor
Cohen (1984) evaln.	300-1000		$2x10^{-12}T^{0.6}exp(-3680/T)$	2.5
Herron, Huie (1973)	298-650		$4.2x10^{-11}exp(-3200/T)$	1.3
evaln.	298		$9.1x10^{-16}$	
	1000		$1.7x10^{-12}$ (extrapolation)	1.5

Comments and Recommendations

We suggest the use of the rate expression of Cohen under combustion conditions (>500 K). The estimated uncertainty is a factor of 2. However, at lower temperatures the results of Herron and Huie are in closer accord with experiments.

(R. F. Hampson, October 1984)

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Cohen, N., "The Use of Transition State Theory to Extrapolate Rate Coefficient for Reactions of O-Atoms with Alkanes," Aerospace Report No ATR-84(7073)-1 August 1984

Herron, J. T., and Huie, R. E., "Rates of Reaction of Atomic Oxygen, II. Some C_2 to C_8 Alkanes," J. Phys. Chem. <u>73</u>, 3327 (1969)

Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data <u>2</u>, 467 (1973)

Westenberg, A. A., and deHaas, N., "Atom-Molecule Kinetics at High Temperature Using ESR Detection. Technique and Results for $O + H_2$, $O + CH_4$, and $O + C_2H_6$," J. Chem. Phys. <u>46</u>, 490 (1967)

Westenberg, A. A., and deHaas, N., "Reinvestigation of the Rate Coefficients for $O + H_2$ and $O + CH_4$," J. Chem. Phys. <u>50</u>, 2512 (1969)

11,6 $C_2H_6 + OH \rightarrow C_2H_5 + H_2O$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
log K_p = 3.42 - 0.4 log T + 4013/T				
Cohen, Westberg (1983) evaln.	300-2000		$3.6x10^{-17}T^{1.9}exp(-570/T)$	
Tully, et al. (1983)	297-800		$1.47x10^{-14}T^{1.04}exp(-913/T)$	1.25

Comments and Recommendations

The expression of Tully et al. (1983) should be used. These data measured by the flash-photolysis-resonance fluorescence technique provide a better data base above room temperature than that used by Cohen and Westberg in their evaluation. It is probably reliable to ±25% at room temperature and to a factor of two at 2000 K.

(R. F. Hampson, May 1983)

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Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data <u>12</u>, 531 (1983)

Tully, F. P., Ravishankara, A. R., and Carr, K., "Kinetic Study of the Reactions of the Hydroxyl Radical with Ethane and Propane," Int. J. Chem. Kinet. <u>15</u>, 1111 (1983)

11,7 $C_2H_6 + HO_2 \rightarrow H_2O_2 + C_2H_5$

Reference	Conditions Temp./K	Conditions [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Baldwin, Walker (1979)	713	$4x10^{17}$ O_2 $8x10^{17}$-$27x10^{17}$ N_2	$2.1x10^{-17}$	2
Walker (1976) review	300-800		$4.9x10^{-13}exp(-7520/T)$	3
Lloyd (1974) review			$1.7x10^{-12}exp(-7050/T)$	upper limit

Comments and Recommendations

Baldwin and Walker's results are derived from a study of the effect of ethane addition on product yields in the oxidation of tetramethylbutane. They are in substantial agreement with the earlier review of Walker. Lloyd's expression is an upper limit and is based on Baldwin's earlier work on H_2-O_2 systems. The expression of Walker is clearly preferred with an uncertainty of a factor of 3.

(W. Tsang, May 1983)

References

Baldwin, R. R., and Walker, R. W., "Rate Constants for Reactions of HO_2 Radicals with Alkanes, Aldehydes, and Related Compounds," Symp. Combust. 17, (Combustion Institute, Pittsburgh, 1979) 525

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169 (1974)

Walker, R. W., "Rate Constants for Reaction in Gas-Phase Hydrocarbon Oxidation", Chapter 7 in "Gas Kinetics and Energy Transfer," A Specialist Periodical Report (The Chemical Society, London, 1977) Vol. 2 pg. 297

12,1 $HCHO \rightarrow H_2 + CO$ (a)
$\rightarrow H + HCO$ (b)

Reference	Conditions Temp./K	Conditions [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Dean, et al. (1980)	1600-3000	$5x10^{18}$ Ar	k_b=$5.5x10^{-8}exp(-40780/T)s^{-1}$	3
Dean, et al. (1978)	1700-2710	2.4-$4.5x10^{18}$ Ar .1, .5, 1.0% HCHO	k_b=$1.3x10^{-8}exp(-37800/T)s^{-1}$ $k_a \sim k_b$	3
Schecker, Jost (1969)	1400-2200	2.1-$8x10^{19}$ Ar .02-1% HCHO	k_b=$8x10^{-8}exp(-36300/T)s^{-1}$	3

Comments and Recommendations

There is considerable uncertainty with respect to the importance of the molecular channel. It has been suggested that the larger rate constant of Schecker and Jost is due to a molecular process (see Just, 1979). Since the chain mechanism which follows bond breaking leads to the same products as the molecular process, in the absence of further details, it is difficult to assess the observation. Berman (PhD Thesis, Lawrence Berkeley Laboratory, University of California, (1981)) has reported on infra-red multiphoton induced decomposition of D_2CO and reported a branching ratio of 10 to 1 in favor of molecular decomposition. The interpretation of the data is, however, difficult. It would appear that there is a molecular channel for decomposition. Its magnitude is uncertain.

We have carried out RRKM calculations and find Dean's results can be reproduced with a downward step size of 300 cm^{-1}, ignoring the molecular channel. Since this step size is comparable with that for other molecules we conclude that the threshold for the molecular channel cannot be lower than that for bond breaking. On this basis the strong collision rate expression for bond breaking is: $k_bo = 2.7x10^9(1/T)^{4.1}exp(-46580/T)s^{-1}$ over the temperature range 1100-2500 K. Collisional efficiencies are given in Table A. For argon with a 300 cm^{-1} step size we derive the rate expression $k_b(0,argon) = 1.9x10^{17}T^{-6.9}exp(-48590/T)s^{-1}$. For larger polyatomics a 1000 cm^{-1} step size is used to obtain $k_b(0,HCHO)=6.3x10^{16}T^{-6.5}exp(-48930/T)s^{-1}$ The estimated uncertainty is a factor of 3.

Table A. Collision efficiency β_c as a function of downward step size and temperature for process b.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
1100	0.021	0.064	0.16	0.33	0.53
1300	0.015	0.048	0.13	0.28	0.48
1500	0.0112	0.037	0.10	0.24	0.43
1700	$8.7x10^{-3}$	0.029	0.085	0.21	0.39
1900	$6.8x10^{-3}$	0.023	0.07	0.17	0.35
2100	$5.4x10^{-3}$	0.019	0.058	0.15	0.31
2300	$4.4x10^{-3}$	0.015	0.049	0.13	0.28
2500	$3.6x10^{-3}$	0.013	0.041	0.11	0.25

(W. Tsang, October 1983)

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Dean, A. M., Johnson, R. L., and Steiner,D. C., "Shock-Tube Studies of Formaldehyde Oxidation," Combust. Flame 37, 41 (1980)

Dean, A. M., Craig, B. L., Johnson, R. L., Schultz, M. C., and Wang, E. E., "Shock Tube Studies of Formaldehyde Pyrolysis," Symp. Combust. 17, (Combustion Institute, Pittsburgh, 1979) 577

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Schecker, H. G., and Jost, W., "Zum Homogenen Thermischen Zerfall von Formaldehyd", Ber. Bunsenges. Physik. Chem. 74, 521 (1969)

12,3 $HCHO + O_2 \rightarrow HO_2 + CHO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Baldwin, et al. (1974)	713-813	0.7-$6x10^{15}$ HCHO 1-$8x10^{17}$ O_2 0-$2.7x10^{18}$ N_2	$3.4x10^{-11}exp(-19600/T)$	2

Comments and Recommendations

The results are derived from studies on the oxidation of formaldehyde in KCl-coated vessels under conditions where the chain length is unity. The uncertainty is estimated to be a factor of 2.

(W. Tsang, May 1983)

References

Baldwin, R. R., Fuller, A. R., Longthorn, D., and Walker, R. W., "Oxidation of Formaldehyde in KCl-coated Vessels," J. Chem. Soc., Faraday Trans. I 70, 1257 (1974)

12,4 $HCHO + H \rightarrow H_2 + CHO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Klemm (1979)	264-479	$3x10^{18}$-$1.5x10^{19}$ He	$3.3x10^{-11}exp(-1848/T)$	1.2
Westenberg, deHaas (1972)	297-652	$1.4x10^{16}$-$7x10^{16}$ He	$2.2x10^{-11}exp(-1893/T)$	1.5
Dean, et al. (1980)	1700-2500	$5x10^{18}$ Ar	$5.5x10^{-10}exp(-5280/T)$	3
Ridley, et al. (1972)	297	$8x10^{17}$ Ar	$5.4x10^{-14}$	1.2

Comments and Recommendations

The rate expression of Klemm is preferred. All low temperature results are in substantial agreement. Using this as a base we fit the results using transition state frequencies as defined from BEBO calculations and obtained the rate expression over all temperatures: $k = 3.64x10^{-16}T^{1.77}exp(-1510/T)cm^3molecule^{-1}s^{-1}$. This results in rate constants that are about a factor of 3 higher than the measurements of Dean et al. Their rate constants are dependent upon the rate of formaldehyde decomposition and probably have uncertainties of this magnitude. The uncertainties are 30% up to 500 K, increasing to a factor of 3 at 2500 K.

(W. Tsang, May 1983)

References

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Klemm, R. B., "Absolute Rate Parameters for the Reactions of Formaldehyde with O Atoms and H Atoms Over the Temperature Range 250-500 K," J. Chem. Phys. 71, 1987 (1979)

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12,5 HCHO + O → HCO + OH

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Chang, Barker (1979)	296-437	4×10^{16} He	$3.8\times10^{-11}\exp(-1583/T)$	1.2
Klemm (1979)	250-498	$1-6\times10^{18}$ Ar	$2.8\times10^{-11}\exp(-1525/T)$	1.2
Klemm, et al. (1980)	298-750	$6-15\times10^{16}$ He	$3.0\times10^{-11}\exp(-1554/T)$	1.2
NASA (1985) evaln.	298-750		$3.0\times10^{-11}\exp(-1550/T)$	1.2
	298		1.6×10^{-13}	1.25

Comments and Recommendations

The expression given in the NASA (1985) evaluation is recommended for the temperature range 250-750 K. It should be reliable to ±25% at room temperature and to ±60% at 750 K. It is based on the results of the three recent studies listed above. It should be noted that Chang and Barker (1979), on the basis of their observation of CO_2 formation at very short reaction time, suggest that 30% of the total reaction may proceed by an addition mechanism to give HCO_2 + H. Independent confirmation is needed.
(R. F. Hampson, May 1983)

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Chang, J. S., and Barker, J. R., "Reaction Rate and Products for the Reaction $O(^3P) + H_2CO$," J. Phys. Chem. 83, 3059 (1979)

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NASA(1985). Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation No. 7, NASA Panel for Data Evaluation, JPL Publication 85-37 July 1985

12,6 $HCHO + OH \rightarrow HCO + H_2O$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
CODATA (1984) eval.	200-425		$1.1x10^{-11}$	1.25 at 298K
Stief, et al. (1980)	228-362	$(6-26)x10^{17}$	$(1.05\pm0.11)x10^{-11}$	1.25
Atkinson, Pitts (1978)	299-426	$16x10^{17}$	$1.25x10^{-11}exp(-88/T)$	1.25
Peeters, Mahnen (1973)	1600	$2.4x10^{17}$	$3.8x10^{-11}$	3
Vandooren, Van	485	$7x10^{17}$	$1.7x10^{-11}$	3
Tiggelen (1977)	570		$2.2x10^{-11}$	3

Comments and Recommendations

The CODATA (1984) recommendation for the temperature range 200-425 is based on the data reported by Stief, et al. (1980) and Atkinson and Pitts (1978). The present evaluation which extends up to 1600 K uses these same data but includes also the higher temperature data of Peeters and Mahnen (1973) and Vandooren and Van Tiggelen (1977). The recommended rate expression is $5.7x10^{-15}T^{1.18}exp(225/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of 25% at 298 K, increasing to a factor of 2 at 1600 K.

(R. F. Hampson, May 1983)

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Stief, L. J., Nava, D. F., Payne, W. A., and Michael, J. V., "Rate Constant for the Reaction of Hydroxyl Radical with Formaldehyde over the Temperature Range 228-362 K," J. Chem. Phys. 73, 2254 (1980)

Vandooren, J., and Van Tiggelen, P. J., "Reaction Mechanisms of Combustion in Low Pressure Acetylene-Oxygen Flames," Symp. Combust. 16, (Combustion Institute, Pittsburgh, 1977) 1133

12,7 $HCHO + HO_2 \rightarrow H_2O_2 + CHO$ (a)
$\rightarrow HO_2CH_2O$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Su, et al. (1979)	298	$2.4x10^{19}$	$k_b=1x10^{-14}$	
Walker (1975) review			$k_a=3.3x10^{-12}exp(-5870/T)$	3
Lloyd (1974) review			$k_a=1.7x10^{-12}exp(-4030/T)$	

Comments and Recommendations

We suggest the use of Walker's rate expression with an uncertainty of a factor of 3. In Su et al.'s system the adduct formed in reaction (b) rearranges and reacts with another HO_2. It should not be important under combustion conditions since it is readily reversible.

(W. Tsang, October 1983)

References

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169 (1974)

Su, F., Calvert, J. G., and Shaw, J. H., "Mechanism of the Photooxidation of Gaseous Formaldehyde," J. Phys. Chem. 83, 3185 (1979)

Walker, R. W., "A Critical Survey of Rate Constants for Reactions in Gas-Phase Hydrocarbon Oxidation," in "Reaction Kinetics," A Specialist Periodical Report (The Chemical Society, Burlington House, London, 1975) Vol. 1, pg.161

13,4 $CO_2 + H \rightarrow CO + OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Baulch, et al. (1976)	1000-3000		$2.5\times10^{-10}\exp(-13300/T)$	1.3

Comments and Recommendations

The rates calculated from the reverse process and the equilibrium constant and rates measured for the forward process are in good agreement.

(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reaction of the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-Containing Species," (Butterworths, London, 1976)

13,5 $CO_2 + O \rightarrow CO + O_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Baulch, et al. (1976) review	1500-3000		$2.8\times10^{-11}\exp(-26500/T)$	3

Comments and Recommendations

The recommended expression is calculated from the expression for the reverse reaction (see data sheet 14,3) and the equilibrium constant.

(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reations, Vol. 3: Homogeneous Gas Phase Reaction of the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-Containing Species," (Butterworths, London, 1976)

14,3 $CO + O_2 \rightarrow CO_2 + O$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Baulch, et al. (1976) review	1500-3000		$4.2 \times 10^{-12} \exp(-24000/T)$	2

Comments and Recommendations

There have been many studies on reaction systems in which this reaction is important. The kinetics must be deduced from interpretation of complex kinetics. Impurities are known to be important. Baulch's recommendations should be used.

(W. Tsang, October 1984)

References

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reaction of the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-containing Species," (Butterworths, London, 1976)

14,4 $CO + H + M \rightarrow HCO + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^6 molecule^{-2} s^{-1}$	Uncertainty factor
Baulch, et al. (1976)	298-773		$2 \times 10^{-33} \exp(-850/T)$ ($M=H_2$) Relative M-efficiencies: H_2(1.0), Ar(0.7), He(0.7)	
Campbell, Handy (1978)	425	10^{17} N_2	4.0×10^{-34} ($M=N_2$)	2
		10^{17} Ar	2.7×10^{-34} (M=Ar)	
Hochanadel, et al. (1980)	298	2.5×10^{19} CO	1.0×10^{-34} (M=CO)	
		2.5×10^{19} CH_4	1.6×10^{-34} ($M=CH_4$)	1.5
		2.5×10^{19} H_2	1.1×10^{-34} ($M=H_2$)	1.5

Comments and Recommendations

There is considerable uncertainty in the activation energy and rate constants at higher temperatures. Our RRKM calculations for a reaction barrier of 10.9 kJ mol^{-1} for addition yield $k_o = 10^{-31.83}T^{0.03}\exp(-1393/T)\mathrm{cm^3molecule^{-2}s^{-1}}$ (strong collisions). The experimental data are consistent with a downward step size for H_2 ~ 300 cm^{-1}; argon ~ 600 cm^{-1}; CH_4 ~ 1500 cm^{-1}; He ~ 250 cm^{-1}; CO ~ 800 cm^{-1}; and N_2 ~ 800 cm^{-1}. Collisional efficiencies as a function of downward step size and temperature can be found in Table A. The rate expressions for N_2 (800 cm^{-1}) and larger polyatomics (1500 cm^{-1}) are:

$$k_o(N_2) = 1.74\times10^{-27}T^{-1.82}\exp(-1856/T)\mathrm{cm^6molecule^{-2}s^{-1}}$$

$$k_o(\mathrm{poly}) = 2.75\times10^{-29}T^{-1.18}\exp(-1649/T)\mathrm{cm^6molecule^{-2}s^{-1}}$$

The uncertainty is a factor of 3.

Table A. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
300	0.16	0.32	0.52	0.70	0.83
500	0.077	0.19	0.37	0.57	0.74
700	0.044	0.12	0.27	0.46	0.66
900	0.028	0.081	0.20	0.38	0.58
1100	0.019	0.058	0.15	0.31	0.51
1300	0.013	0.042	0.12	0.26	0.45
1500	9.5×10^{-3}	0.032	0.091	0.22	0.40
1700	7.1×10^{-3}	0.024	0.072	0.18	0.35
1900	5.4×10^{-3}	0.019	0.058	0.15	0.31
2100	4.2×10^{-3}	0.015	0.047	0.13	0.28
2300	3.3×10^{-3}	0.012	0.038	0.11	0.24
2500	2.6×10^{-3}	9.5×10^{-3}	0.032	0.091	0.22

(W. Tsang, October 1984)

References

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reaction of the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-Containing Species," (Butterworths, London, 1976)

Campbell, I. M., and Handy, B. J., "Studies of Reactions of Atoms in a Discharge Flow Stirred Reactor. Part 2.-O + H_2 + CO System," J. Chem. Soc. Faraday Trans. I 74, 316 (1978)

Hochanadel, C. J., Sworski, T. J., and Ogren, P. J., "Ultraviolet Spectrum and Reaction Kinetics of the Formyl Radical," J. Phys. Chem. 84, 231 (1980)

14,5 $CO + O + M \rightarrow CO_2 + M$

Reference	Conditions Temp./K	 $[M]$/molecule cm^{-3}	Reaction rate constant, $k/cm^6 molecule^{-2} s^{-1}$	Uncertainty factor
Baulch, et al. (1976)	250-500		$6.5\times10^{-33}\exp(-2184/T)$ (M=CO)	
review	298		Relative M-efficiencies: $N_2(1.0)$, $CO(1.77)$, $CO_2(2.7)$	
Dean, Steiner (1977)	2100-3200	5×10^{18} Ar	1.6×10^{-34}	3
Baldwin, et al. (1972) review	300-3500		$8.3\times10^{-34}\exp(-1510/T)$ (M=Ar) Relative M-efficiencies: Ar(1.0), $N_2(2.0)$, CO(3.0), $CO_2(7)$, $O_2(12)$	
Hardy, et al. (1978)	1300-1500	$(6.6-22)\times10^{18}$ Ar, CO Ar/CO ~ 3	$7.7\times10^{-35}\exp(2290/T)$	3

Comments and Recommendations

The extensive data on this process have been thoroughly reviewed by Baulch, et al. and we recommend their selected values. This reaction is very sensitive to impurities; hence there is a great deal of scatter in the reported rate constants. The rate constant may exhibit pressure dependence at pressure in excess of 1 atm. Uncertainties range from 20% to a factor of 2 from room temperature to 800 K and a factor of 3 at 2500 K. (W. Tsang, October 1984)

References

Baldwin, R. R., Jackson, D, Melvin, A., and Rossiter, B. N., "The Second Limit of Hydrogen + Carbon Monoxide + Oxygen Mixtures," Int. J. Chem. Kinet. 4, 277 (1972)

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reaction of the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-containing Species," (Butterworths, London, 1976)

Dean, A. M., and Steiner, D. C., "A Shock Tube Study of the Recombination of Carbon Monoxide and Oxygen Atoms," J. Chem. Phys. 66, 598 (1977)

Hardy, J. W., Gardiner, W. B., and Burcat, A., "Recombination of Carbon Monoxide and Oxygen Atoms," Int. J. Chem. Kinet. 10, 503 (1978)

14,6 $CO + OH \rightarrow H + CO_2$

Reference	Conditions Temp./K	 $[M]$/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Baulch, et al. (1976)	250-2500		$1.12\times10^{-13}\exp[0.000907\times T]$	1.2-1.5
CODATA (1984)	200-300		1.5×10^{-13} (P<100 torr)	1.2
	298		$1.5\times10^{-13}(1+0.45\ P(atm))$ for P = 100-760 torr air	
NASA (1985)	200-300		$1.5\times10^{-13}(1+0.6\ P(atm))$	1.3
Zellner (1979)	300-2000		$1.18\times10^{-13}\exp(0.00092\times T)$	1.2-1.5

Comments and Recommendations

This is an extensively studied process. The review of Baulch is definitive. The CODATA and NASA recommendations allow for the increase in rate constant found at high pressure and in the presence of O_2. This may be a possible new complication. The expression of Zellner parallels that of Baulch and is recommended. Estimated uncertainties range from 20% at low temperatures to 50% at higher temperatures.

(W. Tsang, May 1983)

References

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reaction of the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-containing Species," (Butterworths, London, 1976)

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

NASA(1985). Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation No. 7, NASA Panel for Data Evaluation, JPL Publication 85-37 July 1985

Zellner, R., "Non-Arrhenius Behavior in Bimolecular Reactions of the OH Radical," J. Phys. Chem. 83, 18 (1979)

14,7 $CO + HO_2 \rightarrow HO + CO_2$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3 molecule^{-1} s^{-1}$	factor
Atri, et al. (1977)	773	$(4-17)x10^{17}$ H_2	$3.2x10^{-17}$ derived from	1.5
		$(4-40)x10^{17}$ O_2	$k(HO_2 + CO)/k^{1/2}(HO_2 + HO_2)$	
		$0-45x10^{17}$ N_2	and $k(HO_2 + HO_2) = 3.3x10^{-12}$	
		$1.5x10^{16}-15x10^{17}$ CO	$1x10^{-10}(-11550/T)$	
Baulch, et al. (1976) review	700-1000		$2.5x10^{-10}exp(-11900/T)$	3
Lloyd (1974) review			$1.7x10^{-13}exp(-5000/T)$	
Burrows, et al. (1979)	298	$6x10^{16}$	$<2x10^{-17}$	upper limit
Graham, et al. (1979)	298	$2.5x10^{19}$ CO	$<2x10^{-19}$	upper limit
Howard (1979)	304	10^{17} He	$<4x10^{-17}$	upper limit
	394		$<6x10^{-17}$	upper limit

Comments and Recommendations

The rate constants in the 700-900 K region are probably accurate to ±50%. There are large uncertainties in the Arrhenius expressions. The results of Baulch et al. and Atri, et al.

are in substantial agreement. We suggest the use of the latter. At room temperature, only upper limits have been reported.

(W. Tsang, May 1983)

References

Atri, G. M., Baldwin, R. R., Jackson, D., and Walker, R. W., "The Reaction of OH Radicals and HO_2 Radicals with Carbon Monoxide," Combust. Flame 30, 1 (1977)

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reaction of the O_2-O_3 System, the CO-O_2-H_2 Systems and of Sulphur-Containing Species," (Butterworths, London, 1976) pg. 263

Burrows, J. P., Cliff, D. I., Harris, G. W., Thrush, B. A., and Wilkinson, J. P. T., "Atmospheric Reactions of the HO_2 Radical Studied by Laser Magnetic Resonance Spectroscopy," Proc. Roy. Soc. London A 368, 463 (1979)

Graham, R. A., Winer, A. M., Atkinson, R., and Pitts, J. N., Jr., "Rate Constant for the Reaction of HO_2 with HO_2, SO_2, CO, N_2O, trans-2-Butene, and 2,3-Dimethyl-2-butene at 300 K," J. Phys. Chem. 83, 1563 (1979)

Howard, C. J., "Temperature Dependence of the Reaction $HO_2 + NO \rightarrow OH + NO_2$," J. Chem. Phys. 71, 2352 (1979)

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169 (1974)

15,1 $HCO + M \rightarrow H + CO + M$

$$\log K_p = 5.24426 - 3980.569/T - 30818/T^2 + 1.97237\times10^7/T^2$$

Comments and Recommendations

There are no direct measurements. Literature numbers are estimates. We have derived the following temperature dependent rate expressions on the basis of the recommended reverse rate (14,4), the equilibrium constant and RRKM calculations. The rate expression for strong colliders is:

$$k(HCO + M \rightarrow H + CO + M) = 1.7\times10^{-8}T^{-0.11}\exp(-10228/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

In the presence of N_2 or small polyatomics species at pressures less than 10 atmospheres we suggest the use of the following rate expressions:

$$k_o(N_2) = 8.5\times10^{-3}T^{-2.14}\exp(-10278/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

$$k_o(\text{poly}) = 8.9\times10^{-4}T^{-1.74}\exp(-10243/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

These are based on downward step sizes of 800 cm^{-1} and 1500 cm^{-1} respectively. For other third bodies see [14,4]. Collisional efficiencies as a function of step size down and temperature can be found in Table A. The uncertainty is a factor of 5.

Table A. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.32	0.52	0.70	0.83
500	0.077	0.19	0.37	0.57	0.74
700	0.044	0.12	0.27	0.46	0.66
900	0.028	0.081	0.20	0.38	0.58
1100	0.019	0.058	0.15	0.31	0.51
1300	0.013	0.042	0.12	0.26	0.45
1500	$9.5x10^{-3}$	0.032	0.091	0.22	0.40
1700	$7.1x10^{-3}$	0.024	0.072	0.18	0.35
1900	$5.4x10^{-3}$	0.019	0.058	0.15	0.31
2100	$4.2x10^{-3}$	0.015	0.047	0.13	0.28
2300	$3.3x10^{-3}$	0.012	0.038	0.11	0.24
2500	$2.6x10^{-3}$	$9.5x10^{-3}$	0.032	0.091	0.22

(W. Tsang, October 1984)

15,2 $HCO + H_2 \rightarrow H_2CO + H$

$\log K_p = -1.24219 - 3388.29/T + 22256/T^2 - 0.39111x10^7/T^3$

Comments and Recommendations

There are no direct measurements of this rate constant. By means of the equilibrium constant and the rate of the reverse reaction $H + H_2CO \rightarrow H_2 + HCO$[12,4] we suggest $k = 3x10^{-18}T^2exp(-8972/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 5.

(W. Tsang, May 1983)

15,3 $HCO + O_2 \rightarrow HO_2 + CO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
CODATA (1984) evaln.	300-500		$3.5x10^{-12}exp(140/T)$	1.4
	298		$5.6x10^{-12}$	
Peeters, Mahnen (1973)	1400-1800	$2.4x10^{17}$ (methane flame)	$5x10^{-11}$	10

Comments and Recommendations

The experimental results at room temperature are of high quality. The temperature dependence given in the CODATA (1984) recommendation has been derived from the data of Veyret and Lesclaux. The results at high temperature (>1000 K) are probably uncertain to an order of magnitude. We suggest use of the rate expression: $8.5\times10^{-11}\exp(-850/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. The uncertainties are a factor of 1.5 at room temperature and a factor of 5 at 1500 K.

(W. Tsang, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Peeters, J., and Mahnen, G., "Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames," Symp. Combust. 14, (Combustion Institute, Pittsburgh, Pa., 1973) 133

Veyret, B., and Lesclaux, R., "Absolute Rate Constants for the Reactions of HCO with O_2 and NO from 298 to 503 K," J. Phys. Chem. 85, 1918 (1981)

15,4 $HCO + H \rightarrow H_2 + CO$ (a)
$\rightarrow HCHO$ (b)

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
Reilly, et al. (1978)	298	3×10^{17}	$k_a = 5.5\times10^{-10}$	2
Nadtochenko, et al. (1979)	298	$(0.3-5)\times10^{18}$	$k_a = 2\times10^{-10}$	1.4
Hochanadel, et al. (1980)	298	$(0.4-7)\times10^{19}$	$k_a = 1.1\times10^{-10}$	1.25

Comments and Recommendations

The value of $k(HCO + H \rightarrow H_2 + CO) = 2\times10^{-10}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ is recommended and is probably good to a factor of 2. The formaldehyde forming process will be in the termolecular region [see data sheet on formaldehyde decomposition] and therefore cannot compete.

(W. Tsang, May 1983)

References

Hochanadel, C. J., Sworski, T. J., and Ogren, P. J., "Ultraviolet Spectrum and Reaction Kinetics of the Formyl Radical," J. Phys. Chem. 84, 231 (1980)

Nadtochenko, V. A., Sarkisov, O. M., and Vedeneev, V. I., "Study of the Reactions of the HCO Radical by the Intraresonator Laser Spectroscopy Method During The Pulse Photolysis of Acetaldehyde," Bull. Acad. Sci. USSR, Div. Chem. Sci. 28, 605 (1979) tr. of Izv. Akad. Nauk SSSR, Ser. Khim., 651 (1979)

Reilly, J. P., Clark, J. H., Moore, C. B., and Pimentel, G. C., "HCO Production, Vibrational Relaxation, Chemical Kinetics, and Spectroscopy Following Laser Photolysis of Formaldehyde," J. Chem. Phys. 69, 4381 (1978)

15,5 $HCO + O \rightarrow H + CO_2$ (a)
$\rightarrow OH + CO$ (b)

Comments and Recommendations

There are no direct measurements of the rate of this reaction. The rate constant should be near the collisional value, approximately $5 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 3. The mechanism is assumed to involve addition to a radical site and then decomposition of the activated molecule or direct abstraction, (a). A less exothermic abstraction channel (b) may also make a contribution. Rate constants should be comparable.

(W. Tsang, May 1983)

15,6 $HCO + OH \rightarrow H_2O + CO$

Comments and Recommendations

In the absence of direct measurements we estimate that this process will proceed at close to a collisional rate constant of $\sim 5 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, May 1983)

15,7 $HCO + HO_2 \rightarrow OH + H + CO_2$

Comments and Recommendations

There are no direct measurements for the rate of this process. We assume that the addition mechanism followed by rapid breakdown of the hot adduct will proceed at close to a collisional rate constant of $\sim 5 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ and be an order of magnitude or more faster than the abstraction process. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

15,8 $HCO + H_2O_2 \rightarrow H_2CO + HO_2$

$\log K_p = -1.03519 + 683.21/T + 80888.6/T^2 + 0.55840 \times 10^7/T^3$

Comments and Recommendations

In the absence of direct measurements we have calculated a rate constant expression on the basis of the equilibrium constant and the rate expression for the reverse process. The derived expression is $1.7 \times 10^{-13} \exp(-3486/T) cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 5.

(W. Tsang, May 1983)

15,9 $HCO + H_2O \rightarrow H_2CO + OH$

$\log K_p = -0.47192 - 6927.09/T + 131068.8/T^2 - 2.14989\times10^7/T^3$

Comments and Recommendations

There are no direct measurements on this system. the recommended value is $3.9\times10^{-16}T^{1.35}\exp(-13146/T)\mathrm{cm^3molecule^{-1}s^{-1}}$ with an uncertainty of a factor of 5. It is derived from the recommendation for the reverse reaction $H_2CO + OH \rightarrow HCO + H_2O$ (see data sheet 12,6) and the expression for the equilibrium constant.

(R. F. Hampson, May 1983)

15,10 $HCO + CH_4 \rightarrow CH_3 + H_2CO$

$\log K_p = 0.268020 - 3575.39/T - 11385/T^2 + 0.323819\times10^7/T^3$

Comments and Recommendations

In the absence of direct experimental measurements we have calculated the rate constant on the basis of the reverse process and the equilibrium constant. This yields $k(CHO + CH_4 \rightarrow CH_3 + HCO) = 1.21\times10^{-20}T^{2.85}\exp(-11330/T)\mathrm{cm^3molecule^{-1}s^{-1}}$ with an estimated uncertainty of a factor of 5.

(W. Tsang, May 1983)

15,11 $HCO + C_2H_6 \rightarrow H_2CO + C_2H_5$

$\log K_p = 0.58418 - 2553.42/T - 16450/T^2 + 1.0426\times10^6/T^3$

Comments and Recommendations

In the absence of measurements we have calculated the rate constant on the basis of the estimated rate parameters for the reverse process [17,12] and the equilibrium constant. This leads to $k = 7.8\times10^{-20}T^{2.72}\exp(-9176/T)\mathrm{cm^3molecule^{-1}s^{-1}}$ with an estimated uncertainty of a factor of 5.

(W. Tsang, May 1983)

15,15 $HCO + HCO \rightarrow H_2CO + CO$ (a)
$\rightarrow H_2 + 2CO$ (b)
$\rightarrow (HCO)_2$ (c)

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	$[M]$/molecule cm^{-3}		
Horowitz, Calvert (1978)	298	$(3\text{-}35)x10^{16}$ HCHO $(3\text{-}35)x10^{16}$ C_4H_8	$k_c < k_{a+b}$ $k_a/k_b \sim 5.8$	
Clark, et al. (1978)	298	$30x10^{16}$ HCHO	k_a, only reaction photolysis of HCHO	
Morrison, Heicklen (1979)	296	$0\text{-}60x10^{16}$ NO	k_a only reaction photolysis of HCHO	
Quee, Thyne (1967)	303-376	$(3\text{-}15)x10^{17}$ methyl formate	k_b main reaction $\sim 3.5x10^{-11}$ $k_c \sim 2.5x10^{-13}$	3
Reilly, et al. (1978)	298	$3x10^{17}$	$3x10^{-11}$	3
Nadtochenko, et al. (1979)	298	$(0.3\text{-}5)x10^{18}$	$3x10^{-11}$	1.4
Hochanadel, et al. (1980)	298	$(0.4\text{-}7)x10^{19}$	$2.3x10^{-11}$	1.2
Mulenko (1981)	298	$(0.1\text{-}3)x10^{18}$	$3.6x10^{-11}$	1.2

Comments and Recommendations

There appears to be general consensus that the direct combination is unimportant. The more recent results favor the disproportionation process as the main reaction. We suggest a value of $k(HCO + HCO \rightarrow H_2CO + CO) = 3x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of 50% and $k_a/k_b \sim 5.8$ in accordance with the results of Horowitz and Calvert.
(W. Tsang, May 1983)

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16,2 $CH_3 + H_2 \rightarrow CH_4 + H$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3 molecule^{-1} s^{-1}$	factor
Kerr, Parsonage (1976) review	370-700		$1.4\times10^{-12}\exp(-5488/T)$	
Clark, Dove (1973)	1340	5×10^{18} Ne	7.6×10^{-14}	
Walker (1968) review			$5.5\times10^{-12}\exp(-6143/T)$	
Marshall, Shahkar (1981)	584-671	$(1-4)\times10^{17}$	$8.3\times10^{-13}\exp(-5290/T)$	

Comments and Recommendations

This is an extensively studied reaction. Unfortunately it has been established that the ratio of rates for this process and that of the equally well studied reverse process do not reproduce the equilibrium constant for the reaction. There is also an uncertainty regarding the curvature of the Arrhenius plot. Our recommended rate expression is $4.8\times10^{-22}T^{3.12}\exp(-4384/T) cm^3 molecule^{-1} s^{-1}$ with an uncertainty of 50% at temperatures up to 700 K and a factor of 3 at 2500 K. It is based on a best fit of available experimental results. However, if we combine this rate expression with that for the equally well characterized reverse reactions [10,4] we obtain a heat of reaction that is 4 kJ mol^{-1} lower than that calculated on the basis of the well established thermodynamics. Additional work is needed. This reaction is not important at combustion temperatures.

(W. Tsang, May 1983)

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16,3 $CH_3 + O_2 \rightarrow CH_3O_2$ (a)
$\rightarrow CH_3O + O$ (b)
$\rightarrow CH_2O + OH$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Hsu, et al. (1983)	1150-1560	$(1.8-4.5)\times10^{18}$ Ar 0.21-0.40% azomethane in O_2	$k_b = 1.67\times10^{-10}\exp(-15500/T)$	2
Bhaskaran, et al. (1980)	1700-2300	$(6-9)\times10^{18}$ Ar 5-10 ppm C_2H_6 250-5000 ppm O_2	$k_b = 1.16\times10^{-11}\exp(-12910/T)$ $k_c < 8.6\times10^{-11}\exp(-17400/T)$	2
Klais, et al. (1979)	368	$(0.26-2.6)\times10^{17}$ Ar, Azomethane, O_2	$k_c < 3\times10^{-16}$	
Baldwin, Golden (1978)	1200	8×10^{12}	$k_c < 5\times10^{-17}$	
Parkes (1977)	298	$(0.6-24)\times10^{18}$ N_2, Neopentane	$k_a^0 = 3.1\times10^{-31}$ (N_2) $k_a^\infty = 1.2\times10^{-12}$	1.3
Laufer, Bass (1975)	300	$(1.6-23)\times10^{18}$, He, Ne, Ar	$k_a^\infty = 1.7\times10^{-12}$	1.3
Basco, et al. (1972)	295	$(0.8-11)\times10^{18}$ N_2, Neopentane	$k_a^\infty = 5\times10^{-13}$ $k_a^0 = 1\times10^{-30}$ (neopentane) $= 0.25\times10^{-30}$ (Argon) $k_c < 1\times10^{-16}$	1.3
van den Bergh, Callear (1971)	295	$(1-15)\times10^{18}$ Propane	$k_a^\infty \sim 1.8\times10^{-12}$	1.3
Barnard, Cohen (1968)	473-573	$(1.8-3.6)\times10^{18}$ Acetone	$k_a^0 \sim .84-1.47\times10^{-31}$ $cm^6 molecule^{-2} s^{-1}$	large

Comments and Recommendations

$k_a + k_b^\infty$ at room temperature is near 1.3×10^{-12} $cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2. (b) appears to be more important than (c). RRKM calculations neglecting (c) and assuming (b) proceeds through an activated CH_3O_2 intermediate lead to the results for k_{a+b} given in Table A. Strong collisions are assumed. For N_2 and larger polyatomics a step size of the order of 300 cm^{-1} and 1500 cm^{-1} respectively is commensurate with the experimental results. Collision efficiencies as a function of temperature and downward step size can be found in Table B. Table C gives the branching ratio for decomposition versus stabilization. Using the suggested step size we find over the temperature range 700-2500 K:

$$k_a(N_2,\ 0.1) = 2.8\times10^{32}T^{-14.55}exp(-7573/T)$$
$$k_a(N_2,\ 1) = 1.5\times10^{35}T^{-15.01}exp(-8567/T)$$
$$k_a(N_2,\ 10) = 1.23\times10^{39}T^{-15.77}exp(-10440/T)$$

and

$$k_a(CH_3O_2,\ 0.1) = 7.9\times10^{31}T^{-13.93}exp(-8475T)$$
$$k_a(CH_3O_2,\ 1) = 4.5\times10^{34}T^{-14.38}exp(-9851/T)$$
$$k_a(CH_3O_2,\ 10) = 2.2\times10^{36}T^{-14.50}exp(-11510/T)$$

The recommended rate expression for $k_b = 3.3\times10^{-6}(T)^{-1.57}exp(-14710/T)cm^3molecule^{-1}s^{-1}$ and has been scaled to reproduce the results of Hsu et al. and Bhaskaran et al. It is independent of pressure over most applicable ranges and requires $CH_3O + O$ to be collisional. The uncertainties are a factor of 3.

Table A. Values of $\log(k_{a+b}/k_{a+b}^\infty)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.79	-2.26	-2.61	-2.13	-3.17	-3.12	-2.77	-2.37	-2.07	-1.85	-1.68	-1.56
16.5	-1.37	-1.81	-2.15	-2.46	-2.71	-2.83	-2.67	-2.34	-2.06	-1.85	-1.68	-1.56
17.0	-0.99	-1.39	-1.70	-2.00	-2.25	-2.43	-2.46	-2.27	-2.03	-1.83	-1.67	-1.55
17.5	-0.66	-1.00	-1.29	-1.56	-1.80	-2.00	-2.13	-2.09	-1.95	-1.80	-1.65	-1.54
18.0	-0.40	-0.67	-0.91	-1.16	-1.38	-1.57	-1.74	-1.80	-1.78	-1.70	-1.59	-1.50
18.5	-0.21	-0.40	-0.59	-0.80	-0.99	-1.17	-1.25	-1.44	-1.49	-1.50	-1.45	-1.41
19.0	-0.09	0.21	-0.34	-0.50	-0.66	-0.80	-0.87	-1.06	-1.14	-1.20	-1.21	-1.21
19.5	-0.04	-0.10	-0.17	-0.29	-0.39	-0.51	-0.63	-0.71	-0.79	-0.81	-0.90	-0.93
20.0	-0.01	-0.04	-0.07	-0.14	-0.24	-0.28	-0.36	-0.42	-0.49	-0.54	-0.58	-0.61
20.5		-0.01	-0.02	-0.06	-0.09	-0.13	-0.19	-0.21	-0.25	-0.29	-0.32	-0.34
21.0			-0.01	-0.02	-0.03	-0.05	-0.08	-0.09	-0.11	-0.13	-0.14	-0.16

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.29	0.49	0.68	0.82
500	0.056	0.15	0.31	0.51	0.69
700	0.028	0.081	0.20	0.38	0.58
900	0.014	0.045	0.12	0.27	0.47
1100	$7.8x10^{-3}$	0.026	0.078	0.19	0.36
1300	$4.3x10^{-3}$	0.015	0.047	0.13	0.28
1500	$2.3x10^{-3}$	$8.5x10^{-3}$	0.028	0.083	0.20
1700	$1.3x10^{-3}$	$4.7x10^{-3}$	0.017	0.052	0.14
1900	$6.9x10^{-4}$	$2.6x10^{-3}$	$9.5x10^{-3}$	0.032	0.091
2100	$3.7x10^{-4}$	$1.4x10^{-3}$	$5.3x10^{-3}$	0.018	0.057
2300	$2.0x10^{-4}$	$7.7x10^{-4}$	$2.9x10^{-3}$	0.010	0.035
2500	$9.3x10^{-5}$	$3.6x10^{-4}$	$1.4x10^{-3}$	$5.2x10^{-3}$	0.018

Table C. Branching ratio k_b/k_a as a function of temperature and pressure.

log[M]	T/K								
	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	0.003	0.10	1.13	7.11	29	86	201	391	660
16.5	0.001	0.03	0.37	2.3	9.3	28	64	124	210
17.0		0.01	0.12	0.76	3.0	8.9	21	40	67
17.5		0.004	0.04	0.25	1.0	2.9	6.7	13	22
18.0			0.015	0.09	0.35	0.99	2.2	4.2	7
18.5			0.006	0.03	0.13	0.35	0.77	1.4	2.3
19.0			0.003	0.014	0.05	0.13	0.28	0.51	0.91
19.5			0.001	0.006	0.02	0.05	0.11	0.19	0.30
20.0				0.003	0.01	0.024	0.046	0.08	0.11
20.5				0.0015	0.004	0.01	0.02	0.03	0.05
21.0					0.002	0.005	0.01	0.015	0.02

(W. Tsang, October 1984)

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16,4 $CH_3 + H \rightarrow CH_4$

Reference	Conditions		Reaction rate constant,	Uncertainty
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Sworski, et al. (1980)	296	$25x10^{18}$	$2x10^{-10}$	1.3
Patrick, et al. (1980)	300	$(1.7-30)x10^{17}$ Ar, SF_6	$k\infty = 1.5x10^{-10}$	1.4
Cheng, et al. (1977)	308	$9.4x10^{17}$ C_2H_6	$0.52x10^{-10}$	
		$3.1x10^{18}$	$1.83x10^{-10}$	
		$9.4x10^{18}$	$2.49x10^{-10}$	1.5
		$25.1x10^{18}$	$2.72x10^{-10}$	
		$72.2x10^{18}$	$3.0x10^{-10}$	
Camilleri, et al. (1974)	500-750	$1.3x10^{17}$ Ar	$1.8x10^{-12}$	
		$1.95x10^{17}$	$2.6x10^{-12}$	2
		$2.6x10^{17}$	$3.6x10^{-12}$	
Pratt, Veltman (1974)	295	$(2-5)x10^{17}$ He	$(2.9-7.2)x10^{-12}$	2
Michael, et al. (1973)	300	$2.4x10^{16}$ He	$2.0x10^{-12}$	2
		$5.2x10^{16}$	$2.5x10^{-12}$	
		$8.1x10^{16}$	$5.5x10^{-12}$	
		$1.1x10^{17}$	$8.0x10^{-12}$	
		$1.4x10^{17}$	$5.5x10^{-12}$	
Teng, Jones (1972)	303-603	$2x10^{16}$ H_2	$0.20x10^{-11}exp(-25/T)$	2
Halstead, et al. (1970)	290	$2.7x10^{17}$ Ar	$0.38x10^{-11}$	
		$4.0x10^{17}$	$0.5x10^{-11}$	
		$5.4x10^{17}$	$0.67x10^{-11}$	
Dodonov, et al. (1969)	293	$2.2x10^{17}$ He	$1.7x10^{-11}$	3
Brown, et al. (1966)	298	$(5-10)x10^{16}$ Ar	$3.3x10^{-12}$	3

Comments and Recommendations

The results of Cheng et al., Patrick, et al. and Sworski, et al. have been combined with the reverse rate determination of Chen, et al. to derive the rate expression $k\infty = 10^{-8.7}(1/T)^{0.4}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. For weak collisional effects, the step sizes down for larger polyatomics are in the 1000-2000 cm^{-1} range between 300-1100 K. This leads to the following $k/k\infty$ ratios at 0.1, 1 and 10 atm:

$$\log(k(CH_4,\ 0.1)/k\infty) = 0.174 - 1.104\times10^{-3}T + 1.82\times10^{-8}T^2$$
$$\log(k(CH_4,\ 1)/k\infty) = 0.155 - 4.391\times10^{-3}T - 1.119\times10^{-7}T^2$$
$$\log(k(CH_4,\ 10)/k\infty) = 0.021 + 2.031\times10^{-5}T - 1.161\times10^{-7}T^2$$

For argon, a downward step size of 600 cm^{-1} fits the data from 1200 to 2500 K. The $k/k\infty$ ratios at 0.1, 1, and 10 atm are:

$$\log(k(A,\ 0.1)/k\infty) = 0.225 - 1.652\times10^{-3}T + 1.038\times10^{-7}T^2$$
$$\log(k(A,\ 1)/k\infty) = 0.275 - 8.745\times10^{-4}T - 7.107\times10^{-8}T^2$$
$$\log(k(A,\ 10)/k\infty) = 0.107 - 1.743\times10^{-4}T - 1.927\times10^{-7}T^2$$

In the temperature range 300-700 K the step size for deactivation by rare gases appears to be in the range of 100-200 cm^{-1}. Table A contains data on fall-off behavior for strong colliders. Collision efficiencies as a function of step size can be found in Table B. The estimated uncertainties are a factor of 1.5 near room temperature increasing to a factor of 3 at 2500 K.

Table A. Values of $\log(k/k\infty)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.66	-1.81	-1.96	-2.11	-2.26	-2.40	-2.55	-2.68	-2.81	-2.93	-3.05	-3.16
16.5	-1.23	-1.37	-1.51	-1.66	-1.80	-1.94	-2.09	-2.21	-2.35	-2.47	-2.58	-2.69
17.0	-0.84	-0.97	-1.1	-1.24	-1.38	-1.51	-1.65	-1.78	-1.91	-2.02	-2.13	-2.24
17.5	-0.52	-0.63	-0.75	-0.88	-1.01	-1.13	-1.26	-1.38	-1.50	-1.61	-1.71	-1.81
18.0	-0.28	-0.37	-0.47	-0.58	-0.69	-0.80	-0.92	-1.03	-1.14	-1.24	-1.33	-1.42
18.5	-0.13	-0.19	-0.27	-0.35	-0.44	-0.53	-0.63	-0.73	-0.82	-0.91	-0.99	-1.07
19.0	-0.05	-0.09	-0.14	-0.19	-0.26	-0.33	-0.41	-0.48	-0.56	-0.63	-0.70	-0.77
19.5	-0.02	-0.04	-0.06	-0.09	-0.14	-0.18	-0.24	-0.29	-0.35	-0.41	-0.46	-0.51
20.0	-0.01	-0.01	-0.02	-0.04	-0.06	-0.09	-0.12	-0.16	-0.20	-0.24	-0.27	-0.31
20.5			-0.01	-0.02	-0.02	-0.04	-0.06	-0.08	-0.10	-0.12	-0.14	-0.17
21.0				-0.01	-0.01	-0.01	-0.02	-0.03	-0.04	-0.05	-0.06	-0.08

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.32	0.53	0.71	0.83
500	0.08	0.19	0.37	0.58	0.74
700	0.05	0.13	0.27	0.47	0.66
900	0.03	0.09	0.21	0.39	0.59
1100	0.02	0.06	0.16	0.33	0.53
1300	0.015	0.046	0.13	0.27	0.47
1500	0.011	0.035	0.11	0.23	0.42
1700	0.009	0.029	0.085	0.20	0.39
1900	0.006	0.021	0.065	0.17	0.33
2100	0.005	0.017	0.053	0.14	0.30
2300	0.004	0.014	0.044	0.12	0.27
2500	0.003	0.011	0.037	0.10	0.24

(W. Tsang, October 1984)

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16,5 $CH_3 + O \rightarrow HCHO + H$ (a)
$\rightarrow HCO + H_2$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Hoyermann, Sievert (1979)	300	$(0.64\text{-}3.2)\times10^{15}$ He	$k_a/k_b > 5$	1.2
Walker (1976) review	300-2000		1.6×10^{-10}	1.3
CODATA (1984) evaln.	200-300		1.1×10^{-10}	1.5
Bhaskaran, et al. (1980)	1700-2300	$6\text{-}9)\times10^{18}$ Ar	1.3×10^{-10}	2

Comments and Recommendations

The value of this rate constant is well established at $k_{a+b} = 1.3\times10^{-10}cm^3molecule^{-1}s^{-1}$ with an uncertainty of 50%. (b) is not an important channel. The recent high temperature results of Bhaskaran et al. are based on shock tube decomposition of C_2H_6/O_2 mixtures with direct detection of H and O by atomic resonance absorption spectrometry. Reaction proceeds with a close to collisional rate constant and must involve formation and decomposition of activated molecules. The work of Hoyermann sets an upper limit for reaction channel (b). (W. Tsang, May 1984)

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16,6 $CH_3 + OH \rightarrow CH_3OH$ (a)
$\rightarrow H + CH_2OH$ (b)
$\rightarrow H + CH_3O$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Bhaskaran, et al. (1980)	1700-2300	$(6\text{-}9)\times10^{18}$ Ar	$k_{b+c} = 3.3\times10^{-8}\exp(-13860/T)$	
Sworski, et al. (1980)	300	25×10^{18} CH_4	$k_{a+b+c} = 9.3\times10^{-11}$	

Comments and Recommendations

Hydrogen ejection out of excited CH_3OH represent a possible decomposition channel (b or c). We have performed RRKM calculations on this basis. Thermodynamics and kinetics suggest that step b is more likely than c. We suggest k_{a+b}^{∞} $9x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of 50%. Assuming strong collisions, the pressure dependence of k_{a+b} can be found in Table A. Results for the branching ratio are in Table B. Weak collision effects can be derived from Table C. Note that we have not been able to reproduce the temperature dependence of Bhaskaran et al., but agreement on absolute rates is fairly good.

Using a step size down for CH_3OH of 1000 cm^{-1} at 0.1, 1 and 10 atm we suggest:

$k_b/k_a(CH_3OH, 0.1) = 10^{-21.06}T^{6.91}exp(540/T)$

$k_b/k_a(CH_3OH, 1) = 10^{-17.1}T^{5.55}exp(-508/T)$

$k_b/k_a(CH_3OH, 10) = 10^{-15.9}T^{5.03}exp(-1180/T)$

Assuming for N_2 a step size down of 450 cm^{-1}, at 0.1, 1 and 10 atms:

$k_b/k_a(N_2, 0.1) = 10^{-24.13}T^{7.95}exp(1020/T)$

$k_b/k_a(N_2, 1) = 10^{-19.7}T^{6.4}exp(-20/T)$

$k_b/k_a(N_2, 10) = 10^{-16.8}T^{5.4}exp(-976/T)$

over the temperature range of 700-2500 K. At lower temperatures k_a predominates. The uncertainty is a factor of 4.

Table A. Values of $\log(k_{a+b}/k_{a+b}^{\infty})$: dependence on concentration and temperature.

log[M]	T/K										
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.75	-1.12	-1.38	-1.45	-1.35	-1.20	-1.03	-0.99	-0.76	-0.66	-0.58	-0.50
16.5	-0.47	-0.79	-1.05	-1.20	-1.22	-1.14	-1.01	-0.88	-0.75	-0.66	-0.57	-0.50
17.0	-0.27	-0.51	-0.74	-0.92	-1.02	-1.02	-0.95	-0.85	-0.74	-0.65	-0.57	-0.50
17.5	-0.13	-0.30	-0.49	-0.66	-0.78	-0.87	-0.84	-0.80	-0.71	-0.63	-0.56	-0.49
18.0	-0.06	-0.16	-0.29	-0.43	-0.56	-0.67	-0.71	-0.70	-0.66	-0.61	-0.54	-0.48
18.5	-0.03	-0.07	-0.15	-0.26	-0.36	-0.47	-0.54	-0.57	-0.57	-0.54	-0.50	-0.46
19.0	-0.01	0.03	-0.07	-0.14	-0.21	-0.30	-0.38	-0.43	-0.45	-0.46	-0.44	-0.42
19.5		-0.01	-0.03	-0.06	-0.12	-0.17	-0.23	-0.29	-0.32	-0.35	-0.35	-0.35
20.0			-0.01	-0.02	-0.05	-0.10	-0.13	-0.17	-0.20	-0.23	-0.25	-0.27
20.5				-0.01	-0.01	-0.04	-0.06	-0.09	-0.11	-0.14	-0.16	-0.18
21.0						-0.02	-0.03	-0.04	-0.05	-0.07	-0.09	-0.10

Table B. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K 300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	0.0003	0.018	0.18	0.94	3.6	11.0	29.4	70	152	308	585	1052
16.5	0.00016	0.008	0.076	0.38	1.4	4.1	10.8	25	54	108	202	361
17.0	0.0001	0.004	0.035	0.17	0.58	1.7	4.2	9.6	20	39.4	73	129
17.5		0.002	0.018	0.08	0.26	0.72	1.8	3.9	7.8	15.3	28	48
18.0		0.0013	0.0099	0.04	0.13	0.34	0.80	1.7	3.4	6.3	11	19
18.5		0.0007	0.0053	0.022	0.07	0.17	0.39	0.81	1.6	2.8	4.9	8
19.0		0.0003	0.0027	0.011	0.036	0.09	0.20	0.41	0.76	1.3	2.2	3.6
19.5		0.0001	0.0012	0.0058	0.019	0.05	0.11	0.21	0.39	0.67	1.1	1.7
20.0			0.0005	0.0026	0.009	0.02	0.05	0.11	0.20	0.34	0.55	0.84
20.5			0.00017	0.001	0.004	0.01	0.03	0.05	0.10	0.17	0.28	0.43
21.0				0.0003	0.001	0.005	0.01	0.02	0.05	0.08	0.14	0.21

Table C. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
300	0.16	0.32	0.53	0.71	0.84
500	0.077	0.19	0.31	0.57	0.74
700	0.044	0.12	0.19	0.46	0.65
900	0.027	0.08	0.15	0.38	0.58
1100	0.018	0.056	0.11	0.31	0.51
1300	0.012	0.040	0.085	0.25	0.44
1500	8.7×10^{-3}	0.029	0.085	0.20	0.39
1700	6.2×10^{-3}	0.021	0.065	0.16	0.33
1900	4.6×10^{-3}	0.016	0.051	0.14	0.29
2100	3.4×10^{-3}	0.012	0.041	0.11	0.25
2300	2.6×10^{-3}	9.4×10^{-3}	0.031	0.091	0.21
2500	2.0×10^{-3}	7.4×10^{-3}	0.025	0.074	0.18

(W. Tsang, May 1983)

References

Bhaskaran, K. A., Frank, P., and Just, Th., "High Temperature Methyl Radical Reactions with Atomic and Molecular Oxygen," Proc. of 12th Symp. on Shock Tubes and Waves (The Magnes Press, Jerusalem, 1980) 503

Sworski, T. J., Hochanadel, C. J., and Ogren, P. J., "Flash Photolysis of H_2O Vapor in CH_4. H and OH Yields and Rate Constants for CH_3 Reactions with H and OH," J. Phys. Chem. 84, 129 (1980)

16,7 $CH_3 + HO_2 \rightarrow CH_3O + OH$ (a)
$\rightarrow CH_4 + O_2$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Colket, et al. (1977)	1030-1115	$6.8x10^{18}$ N_2 $(0.7-5)x10^{16}$ CH_3CHO $(0.1-5)x10^{17}$ O_2	$k_a = 3.3x10^{-11}$	

Comments and Recommendations

Reaction (a) has been proposed to account for the oxidation of methyl radicals in acetaldehyde oxidation. This reaction involves addition followed by decomposition of the hot adduct. For the abstraction process (b) we estimate $k = 6x10^{-12}cm^3molecule^{-1}s^{-1}$ as calculated from the estimated rate of the reverse process and the equilibrium constant. Uncertainties are a factor of 3 for (a) and 5 for (b).

(W. Tsang, May 1983)

References

Colket, M. B., III, Naegeli, D. W., and Glassman, I., "High-Temperature Oxidation of Acetaldehyde," Symp. Combust. 16, (Combustion Institute, Pittsburgh, 1977) 1023

16,8 $CH_3 + H_2O_2 \rightarrow CH_4 + HO_2$

$\log K_p = -1.303 + 4258.6/T - 69552.6/T^2 + .23452x10^7/T^3$

Comments and Recommendations

In the absence of direct measurements we estimate the rate of this process on the basis of the reverse reaction [10,7] and the equilibrium constant. This leads to $k(CH_3 + H_2O_2 \rightarrow CH_4 + HO_2) = 2x10^{-14}exp(300/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of at least 5. Note that the value for k(10,7) is an estimate and the fact that it leads to a negative activation energy for this, the reverse process, suggests that higher rate parameters may be more appropriate.

(W. Tsang, May 1983)

16,9 $CH_3 + H_2O \rightarrow CH_4 + OH$

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	$[M]/molecule\ cm^{-3}$		
Cohen, Westberg (1983) evaln.	700-3000		$8.0\times10^{-22}T^{2.9}exp(-7480/T)$	1.6

Comments and Recommendations

This recommended value is derived from the recommendation for the rate of the reverse reaction $CH_4 + OH \rightarrow CH_3 + H_2O$ (see data sheet 10,6) and equilibrium constant data.
(R. F. Hampson, May 1983)

References

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

16,11 $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	$[M]/molecule\ cm^{-3}$		
Kerr, Parsonage (1976) review	400-800		$9.33\times10^{-1.3}exp(-5841/T)$	1.3
Clark, Dove (1973) review	400-2000		$9.1\times10^{-25}T^4exp(-4169/T)$	1.3-3

Comments and Recommendations

In order to relate low and high temperature data a curved Arrhenius dependence is necessary. We therefore recommend the expression of Clark and Dove which is based on a BEBO calculation. We estimate the uncertainty to be ±30% at room temperature and a factor of 3 at 2500 K.
(W. Tsang, May 1983)

References

Clark, T. C., and Dove, J. E., "Examination of Possible Non-Arrhenius Behavior in Reactions," Can. J. Chem. 51, 2147 (1973)

Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals," (Butterworths, London, 1976)

16,12 $CH_3 + HCHO \rightarrow CH_4 + CHO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Anastasi (1983)	500-603	$(3-10)x10^{18}$	$1.4x10^{-12}exp(-3490/T)$	1.3
Manthorne, Pacey (1978)	788-935	$(5-35)x10^{17}$	$2.1x10^{-11}exp(-5410/T)$	1.5
Held, et al. (1977)	1005		$5x10^{-14}$	2
Aronowitz, Naegeli (1977)	1063-1223	$7x10^{18}$ N_2	$1.3-7.5x10^{-12}$	3
Kerr, Parsonage (1976) review	300-500		$1.7x10^{-13}exp(-3070/T)$	1.5

Comments and Recommendations

We have adjusted the activation energy of a BEBO calculation to fit the experimental results from 300 to 1005 K. The data of Aronowitz and Naegeli seem high. The recommended rate expression is $k = 9.2x10^{-21}T^{2.81}exp(-2950/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2 from 300-1000 K and increasing to a factor of 3 at 2500 K.

(W. Tsang, May 1983)

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Aronowitz, D., and Naegeli, D., "High Temperature Pyrolysis of Dimethyl Ether," Int. J. Chem. Kinet. 9, 471 (1977)

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Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals," (Butterworths, London, 1976)

Manthorne, K. C., and Pacey, P. D., "The Reaction of Methyl Radicals with Formaldehyde in Dimethyl Ether Pyrolysis," Can. J. Chem. 56, 1307 (1978)

16,14 $CH_3 + CO + M \rightarrow CH_3CO + M$

Reference	Conditions		Reaction rate constant,	Uncertainty
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Anastasi, Maw (1982)	263-343	$(0.3\text{-}2.7)\times10^{19}$ CO		1.3
	263	2.7×10^{19}	1.3×10^{-18}	
	303	3×10^{18}	3.6×10^{-18}	
	303	2.4×10^{19}	7.9×10^{-18}	
	343	3×10^{18}	6.1×10^{-18}	
	343	2.1×10^{19}	16.6×10^{18}	
Parkes (1981)	298	3×10^{18} CO	1.8×10^{-18}	1.3
		2.4×10^{19} CO	6.0×10^{-18}	
Watkins, Word (1974)	260-413	$(1.8\text{-}8)\times10^{19}$ SF_6, CO, azomethane	$k_\infty = 2.5\times10^{-13}\exp(-3000/T)$	1.5
Kerr, Calvert (1965)	300	$(2.4\text{-}7.2)\times10^{18}$ azomethane, CO, neopentane	$k = 6.8\times10^{-15}\exp(-1964/T)$	2

Comments and Recommendations

Results are compatible with the reverse process and the equilibrium constant assuming $\Delta H_f(CH_3CO) \sim 10$ kJ mol at 300 K. We recommend the strong collision expression

$$k_o(CH_3 + CO + M \rightarrow CH_3CO + M) = 10^{-24.5}T^{-2.33}\exp(-3717/T)cm^6molecule^{-2}s^{-1}$$

Corrections from the third order limit and collision efficiencies can be found in Tables A and B. The measurements of Anastasi and Maw and Parkes in CO are commensurate with a downward step size of 300 cm^{-1}. For SF_6 the results of Watkins and Word are consistent with step size of 1000 cm^{-1}. In the temperature range 300-1700 K we suggest the use of the expressions:

$$k(N_2,\ 0) = 10^{-9.4}T^{-7.56}\exp(-5490/T)cm^6molecule^{-2}s^{-1}$$

which, when corrected for pressure effects, leads at 1 and 10 atm N_2 to the following:

$$\log(k(N_2,\ 1)/k(N_2,\ 0)) = -0.536 + 8.681\times10^{-4}T - 3.35\times10^{-7}T^2$$

$$\log(k(N_2,\ 10)/k(N_2,\ 0)) = -1.55 + 2.35\times10^{-3}T - 8.685\times10^{-7}T^2$$

where we have used a step size down of 450 cm^{-1}.

For larger polyatomics the rate expression for strong colliders is

$$k(CH_3O,\ 0) = 10^{-12.6}T^{-6.3}\exp(-5263/T)\ cm^6molecule^{-2}s^{-1}$$

which when corrected for pressure effects at 1 and 10 atoms leads to:

$$\log(k(CH_3CO,\ 1)/k(CH_3CO,\ 0)) = -0.672 + 1.003\times10^{-3}T - 3.662\times10^{-7}T^2$$

$$\log(k(CH_3CO.\ 10)/k(CH_3CO.\ 0)) = -1.727 + 2.335\times10^{-3}T - 7.954\times10^{-7}T^2$$

using a step size of 1500 cm^{-1}. We estimate the uncertainties as a factor of 3.

Table A. Values of $\log k_b o$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
17.0	-0.01	-0.01	-0.01									
17.5	-0.03	-0.02	-0.02	-0.01	-0.01	-0.01						
18.0	-0.08	-0.06	-0.05	-0.04	-0.03	-0.02	-0.02	-0.01	-0.01	-0.01	-0.01	
18.5	-0.18	-0.14	-0.12	-0.09	-0.07	-0.06	-0.04	-0.03	-0.02	-0.02	-0.01	-0.01
19.0	-0.37	-0.29	-0.24	-0.19	-0.15	-0.12	-0.09	-0.07	-0.05	-0.04	-0.03	-0.02
19.5	-0.65	-0.53	-0.42	-0.34	-0.27	-0.21	-0.17	-0.13	-0.10	-0.08	-0.06	-0.05
20.0	-1.03	-0.84	-0.69	-0.56	-0.46	-0.37	-0.29	-0.23	-0.18	-0.15	-0.12	-0.10
20.5	-1.47	-1.25	-1.04	-0.86	-0.72	-0.59	-0.47	-0.40	-0.33	-0.27	-0.22	-0.18
21.0	-1.94	-1.70	-1.46	-1.25	-1.06	-0.90	-0.75	-0.64	-0.54	-0.47	-0.40	-0.34

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.13	0.28	0.48	0.67	0.81
500	$5.2x10^{-2}$	0.14	0.29	0.49	0.68
700	$2.3x10^{-2}$	0.07	0.17	0.35	0.55
900	$1.1x10^{-2}$	$3.5x10^{-2}$	0.10	0.23	0.42
1100	$5.1x10^{-3}$	$1.8x10^{-2}$	0.06	0.15	0.30
1300	$2.4x10^{-3}$	$8.8x10^{-3}$	$3x10^{-2}$	$8.6x10^{-2}$	0.20
1500	$1.1x10^{-3}$	$4.3x10^{-3}$	$1.5x10^{-2}$	$4.8x10^{-2}$	0.13
1700	$5.4x10^{-4}$	$2.0x10^{-3}$	$7.5x10^{-3}$	$2.5x10^{-2}$	$7.6x10^{-2}$
1900	$2.5x10^{-4}$	$9.6x10^{-4}$	$3.6x10^{-3}$	$1.3x10^{-2}$	$4.1x10^{-2}$
2100	$1.1x10^{-4}$	$4.4x10^{-4}$	$1.7x10^{-3}$	$6.3x10^{-3}$	$2.2x10^{-2}$
2300	$5.2x10^{-5}$	$2.0x10^{-4}$	$7.9x10^{-4}$	$3.0x10^{-3}$	$1.1x10^{-2}$
2500	$2.4x10^{-5}$	$9.4x10^{-5}$	$3.7x10^{-4}$	$1.4x10^{-3}$	$5.2x10^{-3}$

(W. Tsang, October 1984)

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16,15 $CH_3 + HCO \rightarrow CH_4 + CO$ (a)
$\rightarrow CH_3CHO$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Quee, Thynne (1967)	303-376	$(3-15)x10^{17}$ methyl formate	$k_a/k_b \sim 5.8$	2
Toby, Kutschke (1959)	353-453	$1x10^{18}$ azomethane $(0.02-0.5)x10^{18}$ HCHO	$k_a/k_b > 4$	2
Nadtochenko, et al. (1979)	298	$(3-60)x10^{18}$	$k = 2.3x10^{-10}$	3
Mulenko (1981)	298	$(0.1-3)x10^{18}$	$k = 4.4x10^{-11}$	

Comments and Recommendations

There seems to be agreement that the disproportionation process is favored. We suggest $k(CH_3+HCO \rightarrow CH_4+CO)=2x10^{-10}cm^3molecule^{-1}s^{-1}$ and $k(CH_3+HCO \rightarrow CH_3CHO)= 3x10^{-11}cm^3molecule^{-1}s^{-1}$ with uncertainties of a factor of 2. We deduce the rate constant for (b) on the basis of the reverse reaction (Colket et al. and references therein), which is typical of radical combination process, and the equilibrium constant. Our RRKM calculations indicate that at low temperatures k_b is very close to the high pressure limit.

(W. Tsang, May 1983)

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16,16 $2CH_3 \rightarrow C_2H_6$ (a)
$\rightarrow C_2H_5 + H$ (b)

Reference	Conditions		Reaction rate constant,	Uncertainty
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3 molecule^{-1} s^{-1}$	factor
$\log K_p = -8.97 + 20017/T - 50209/T^2$				
MacPherson, et al. (1983)	296-577	$(0.83\text{-}162)\times10^{17}$	$k_a{\infty} = 2.78\times10^{-11}\exp(154/T)$ $k_ao = (6\pm3)\times10^{-29}\exp(1680\pm300/T)$	
Baulch, Duxbury (1980)	250-420		$k\infty = 3.98\times10^{-11}$	
Quack, Troe (1977)	250-1400			
review	300		$k\infty = 4.8\times10^{-11}$	
	1400		$k\infty = 2.9\times10^{-11}$	
Roth, Just (1979)	1650-2100	$(1.7\text{-}2.3)\times10^{19}$	$k_b = 1.33\times10^{-9}\exp(-13400/T)$	

Comments and Recommendations

There have been a large number of studies on this reaction. They cover effects arising from pressure as well as temperature. There is considerable disagreement with regard to lower temperature pressure dependence, and there is only one such study at higher temperature. We have combined these results with data for the decomposition process and obtained a best fit of results in the form $k_a{\infty} = 1.68\times10^{-9}(1/T)^{+0.64} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of two at the higher temperatures. The pressure dependence for strong colliders can be found in Table A. Table B contains information on collisional efficiencies as a function of step size down and temperature.

The work of MacPherson et al. was carried out in argon and the fall-off behavior is commensurate with a downward step size of 300 cm^{-1}. This can be compared with a 600 cm^{-1} step size down derived from high temperature recombination rates at 1350 K and shock tube results (as summarized in Baulch and Duxbury) on ethane decomposition. A strong collider (ethane) appears to have a collision efficiency at 900 K commensurate with a 1000 cm^{-1} downward step-size (for the decomposition reaction).

The work of Roth and Just for reaction (b) implies $k(C_2H_5 + H \rightarrow C_2H_6) \approx 6\times10^{-10} cm^3 molecule^{-1} s^{-1}$ or close to an order of magnitude higher than the value at room temperature if reaction proceeds via an activated ethane molecule. The activation energy appears to be high. These results should be used with caution. Our RRKM calculations yield the expression $3\times10^{-12}\exp(-5248.5/T) cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 4. Fortunately this reaction cannot be of any importance in combustion systems except at the highest temperatures.

Our recommended correction factors for Ar (and N_2) at temperatures in excess of 900 K are:

$$\log(k(Ar,\ 0.1)/k\infty) = 1.55 + 9.16\times10^{-4}T - 1.533\times10^{-6}T^2 + 2.61\times10^{-10}T^3$$

$$\log(k(Ar,\ 1)/k\infty) = -0.235 + 1.033\times10^{-3}T - 1.114\times10^{-6}T^2 + 1.425\times10^{-10}T^3$$

$$\log(k(\mathrm{Ar},\ 10)/k_\infty) = -0.151 + 5.55\times10^{-4}T - 4.295\times10^{-7}T^2 - 1.081\times10^{-11}T^3$$

In the presence of ethane at 800-900 K, the reverse decomposition rates suggest that step size in deactivation is of the order of 1000 cm^{-1}. On this basis we recommend:

$$\log(k(C_2H_6,\ 0.1)/k_\infty) = -0.185 + 9.74\times10^{-4}T - 1.31\times10^{-6}T^2 + 2.05\times10^{-10}T^3$$

$$\log(k(C_2H_6,\ 1)/k_\infty) = -0.20 + 8.2\times10^{-4}T - 7.96\times10^{-7}T^2 + 7.45\times10^{-11}T^3$$

$$\log(k(C_2H_6,\ 10)/k_\infty) = -0.087 + 2.88\times10^{-4}T - 1.59\times10^{-7}T^2 - 5.64\times10^{-11}T^3$$

Table A. Values of $\log(k/k_\infty)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.23	-0.45	-0.71	-0.99	-1.25	-1.52	-1.78	-2.03	-2.28	-2.51	-2.73
16.5	-0.03	-0.12	-0.29	-0.49	-0.72	-0.95	-1.19	-1.42	-1.66	-1.89	-2.10	-2.31
17.0	-0.01	-0.06	-0.17	-0.32	-0.50	-0.69	-0.89	-1.10	-1.31	-1.51	-1.71	-1.90
17.5	0.0	-0.03	-0.09	-0.19	-0.32	-0.47	-0.64	-0.81	-0.99	-1.17	-1.35	-1.53
18.0	0.0	-0.01	-0.04	-0.10	-0.19	-0.30	-0.42	-0.57	-0.72	-0.87	-1.03	-1.18
18.5	0.0	0.0	-0.02	-0.05	-0.10	-0.17	-0.26	-0.37	-0.49	-0.61	-0.74	-0.88
19.0	0.0	0.0	-0.01	-0.02	-0.045	-0.09	-0.15	-0.22	-0.31	-0.40	-0.50	-0.61
19.5	0.0	0.0	0.0	-0.01	-0.02	-0.04	-0.07	-0.12	-0.17	-0.24	-0.31	-0.39
20.0	0.0	0.0	0.0	0.0	-0.01	-0.02	-0.03	-0.06	-0.09	-0.13	-0.17	-0.23
20.5	0.0	0.0	0.0	0.0	0.0	-0.01	-0.01	-0.02	-0.04	-0.06	-0.09	-0.12
21.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.01	-0.015	-0.02	-0.04	-0.05

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.31	0.46	0.56	0.65	0.80
500	0.18	0.30	0.40	0.50	0.69
700	0.11	0.20	0.29	0.39	0.59
900	0.07	0.14	0.21	0.30	0.50
1100	0.046	0.093	0.15	0.23	0.42
1300	0.031	0.069	0.11	0.17	0.35
1500	0.022	0.050	0.082	0.13	0.29
1700	0.015	0.036	0.061	0.10	0.23
1900	0.011	0.026	0.044	0.076	0.19
2100	0.0074	0.018	0.032	0.057	0.15
2300	0.0051	0.013	0.023	0.042	0.12
2500	0.0036	0.009	0.017	0.031	0.09

(W. Tsang, October 1984)

References

Baulch, D. L., and Duxbury, J., "Ethane Decomposition and the Reference Rate Constant for Methyl Radical Recombination," Combust. Flame 37, 313 (1980)

MacPherson, M. T., Pilling, M. J., and Smith, M. J. C., "The Pressure and Temperature Dependence of the Rate Constant for Methyl Radical Recombination over the Temperature Range 296-577 K," Chem. Phys. Lett. 94, 430 (1983)

Quack, M., and Troe, J., "Unimolecular Reactions and Energy Transfer of Highly Excited Molecules," Chapter 5 in Gas Kinetics and Energy Transfer, A Specialist Periodical Report (The Chemical Society, London, 1977) Vol. 2 pg. 175

Roth, P., and Just. Th., "Messungen zur Hochtemperaturpyrolyse von Athan," Ber. Bunsenges. Phys. Chem. 83, 577 (1979)

17,1 $C_2H_5 + M \rightarrow C_2H_4 + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Kerr, Lloyd (1968) review			$k\infty = 2.5x10^{14}exp(-20590/T)s^{-1}$ $k_o = 1x10^{-6}exp(-16000/T)$	

Comments and Recommendations

The data on the forward reaction have been combined with results from lower temperature studies on the reverse reaction to derive the rate expression for decomposition at the high pressure limit. The recommended expression is $k\infty = 10^{9.69}T^{1.19}exp(-18722/T)s^{-1}$. The $k/k\infty$ values as a function of pressure and temperature are given in Table A for strong colliders. Collision efficiencies as a function of downward step size and temperature can be found in Table B. On the basis of experiments in the pressure dependent region we find at room temperature downward step sizes of 80 cm^{-1} for H_2, 1000 cm^{-1} for SF_6, 300 cm^{-1} for Kr, 200 cm^{-1} for N_2, 200 cm^{-1} for Ar and, at the higher temperature ranges, 1000 cm^{-1} for ethane. Over the entire temperature range we suggest the use of a 450 cm^{-1} step size down for N_2. This leads to the following fall-off factors:

$$log(k(N_2, 0.1)/k\infty) = .0678 + 3.365x10^{-4}T - 1.844x10^{-6}T^2 + 3.646x10^{-10}T^3$$
$$log(k(N_2, 1)/k\infty) = -.236 + 1.349x10^{-3}T - 1993x10^{-6}T^2 + 3.442x10^{-10}T^3$$
$$log(k(N_2, 10)/k\infty) = -.323 + 1.391x10^{-3}T - 1.457x10^{-6}T^2 + 1.882x10^{-10}T^3$$

For ethyl, a 1000 cm^{-1} step size down leads to the fall-off factors:

$$log(k(C_2H_5, 0.1)/k\infty) = -.051 + 6.73x10^{-4}T - 1.707x10^{-6}T^2 + 3.083x10^{-10}T^3$$
$$log(k(C_2H_5, 1)/k\infty) = -.252 + 1.24x10^{-3}T - 1.56x10^{-6}T^2 + 2.325x10^{-10}T^3$$
$$log(k(C_2H_5, 10)/k\infty) = -.229 + 9.107x10^{-4}T - 8.32x10^{-7}T^2 + 5.016x10^{-11}T^3$$

The overall uncertainty is a factor of 2.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

Log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.67	-0.84	-1.11	-1.45	-1.76	-2.07	-2.38	-2.66	-2.93	-3.18	-3.41	-3.62
16.5	-0.35	-0.51	-0.77	-1.06	-1.36	-1.66	-1.95	-2.22	-2.48	-2.72	-2.94	-3.14
17.0	-0.17	-0.29	-0.50	-0.75	-1.02	-1.29	-1.55	-1.81	-2.05	-2.27	-2.48	-2.68
17.5	-0.06	-0.15	-0.30	-0.51	-0.73	-0.96	-1.20	-1.42	-1.64	-1.85	-2.05	-2.23
18.0	-0.02	-0.07	-0.17	-0.31	-0.49	-0.68	-0.88	-1.07	-1.27	-1.45	-1.63	-1.80
18.5	-0.01	-0.03	-0.08	-0.18	-0.30	-0.44	-0.60	-0.76	-0.93	-1.09	-1.24	-1.39
19.0	-0.01	-0.01	-0.04	-0.09	-0.17	-0.27	-0.38	-0.51	-0.64	-0.77	-0.90	-1.02
19.5	0.0	-0.01	-0.01	-0.04	-0.08	-0.14	-0.21	-0.30	-0.40	-0.50	-0.60	-0.70
20.0	0.0	0.0	0.0	-0.01	-0.03	-0.07	-0.11	-0.16	-0.22	-0.30	-0.36	-0.44
20.5	0.0	0.0	0.0	-0.01	-0.01	-0.03	-0.05	-0.08	-0.11	-0.15	-0.19	-0.24
21.0	0.0	0.0	0.0	0.0	0.0	-0.01	-0.02	-0.03	-0.05	-0.07	-0.09	-0.11

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.30	0.50	0.69	0.82
500	0.063	0.16	0.33	0.53	0.71
700	0.031	0.091	0.22	0.40	0.60
900	0.017	0.053	0.14	0.30	0.50
1100	0.0097	0.032	0.09	0.22	0.40
1300	0.0056	0.020	0.06	0.16	0.32
1500	0.0033	0.012	0.038	0.11	0.24
1700	0.0019	0.007	0.024	0.07	0.18
1900	0.0011	0.004	0.015	0.047	0.13
2100	0.00065	0.0025	0.0089	0.030	0.087
2300	0.00036	0.0014	0.0052	0.018	0.057
2500	0.00021	0.0008	0.003	0.011	0.036

(W. Tsang, October 1984)

References

Kerr, J. A., and Lloyd, A. C., "Decomposition Reactions of Radicals," Quart. Rev. 22, 549 (1968)

17,2 $C_2H_5 + H_2 \rightarrow C_2H_6 + H$

Reference	Conditions		Reaction rate constant,	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3 molecule^{-1} s^{-1}$	
$\log K_p = -1.826 - 834.87/T + 38706/T^2 + 4.954 \times 10^6/T^3$				
Cao, Back (1982)	1111-1200	1.5×10^{18} H_2 10 ppm C_2H_4	$6.7 \times 10^{-11} \exp(-11581/T)$	1.5
Baldwin, et al. (1969)	713	$(1-3) \times 10^{18}$ H_2 4-15% O_2, 2-3% C_2H_5CHO	2.8×10^{-16}	2
Reid, LeRoy (1968)	513-593	$(1.6-6) \times 10^{18}$ H_2 $(2-7) \times 10^{16}$ C_2H_4	$3.8 \times 10^{-12} \exp(-6898/T)$	1.5
Boddy, Steacie (1961)	375-595	$(4-13) \times 10^{17}$ 3-pentanone-d_{10} $(4-9) \times 10^{-17}$ H_2	$3.4 \times 10^{-13} \exp(-5690/T)$	1.5

Comments and Recommendations

The experimental results of Baldwin et al. have been rederived using their ratio for $k(C_2H_5 + O_2)/k(C_2H_5 + H_2)$ and the value for $k(C_2H_5 + O_2)$ (17,3) published in 1980. The data of Reid and LeRoy and those of Boddy and Steacie have been recalculated using newer values for the rate of C_2H_5 recombination [17,17]. No corrections have been made for isotope effects. The results are consistent (to within 50%) with the numbers derived from the reverse rate and equilibrium constant. This leads to $k(C_2H_5 + H_2 \rightarrow C_2H_6 + H) = 10^{-23.29} T^{3.6} \exp(-4253/T) cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 1.5 to 700 K, and greater than 4 at 1200 K. The results of Cao and Back are a factor of 4 slower. The activation energy is very high. The results are based on a number of assumptions. Nevertheless their results raise the possibility that our estimated uncertainty may be too optimistic.

(W. Tsang, May 1983)

References

Baldwin, R. R., Walker, R. W., and Langford, D. H., "Reaction of Ethyl Radicals with Hydrogen and Deuterium," Trans. Faraday Soc. 65, 2116 (1969)

Boddy, P. J., and Steacie, E. W. R., "Hydrogen Atom Abstraction by Ethyl-d_5 Radicals. Part II.," Can. J. Chem. 39, 13 (1961)

Cao, J.-R., and Back, M. H., "Kinetics of the reaction $C_2H_5 + H_2 \rightarrow C_2H_6 + H$ from 1111-1200 K," Can. J. Chem. 60, 3039 (1982)

Reid, L. W., and LeRoy, D. J., "The Mercury (6^3P_1) Photosensitized Hydrogenation of Ethylene. Kinetics of the Reaction $C_2H_5 + H_2 = C_2H_6 + H$," Can. J. Chem. 46, 3275 (1968)

17,3 $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ (a)
$\rightarrow C_2H_4O + OH$ (b)
$\rightarrow C_2H_5O_2$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Baldwin, et al. (1980)	813	$(0.6-6)x10^{18}$ N_2,O_2,H_2,C_2H_6 $(t-C_4H_9)_2$	$k_a = 1.28x10^{-13}$	1.5
			$k_a = 1.4x10^{-12}exp(-1950/T)$	
			$k_b = 1.0x10^{-13}exp(-3450/T)$	
Walker (1975) review	753		$k_a = 9x10^{-14}$	
	896		$k_a = 1.6x10^{-13}$	
Plumb, Ryan (1981)	295	$(2-34)x10^{16}$	$k_a = 2.1x10^{-13}$	2
			$k_c = 4.4x10^{-12}$	5

Comments and Recommendations

The study of Baldwin et al. involved measuring C_2H_4, C_2H_4O, and butane yields in reacting 2,2,3,3-tetramethylbutane-O_2-ethane systems in boric acid coated vessels. When this was combined with earlier work on propionaldehyde oxidation at lower temperature they obtained the rate expressions given above. Rate constants should be good to ±50%. There is probably considerable uncertainty in the temperature dependence. The activation energy should be small. Note that the recent room temperature value of Plumb and Ryan for k_a is a factor of 100 faster than is predicted by extrapolation of the expression based on higher temperature data. At room temperature the addition reaction is much more important than disproportionation. But due to fall-off effects and the weak C-O_2 bond, under combustion conditions disproportionation will be more important. We recommend using the expressions of Baldwin et al. for combustion purposes.

(W. Tsang, May 1983)

References

Baldwin, R. R., Pickering, I. A., and Walker, R. W., "Reactions of Ethyl Radicals with Oxygen over the Temperature Range 400-540 C," J. Chem. Soc., Faraday Trans. I 76, 2374 (1980)

Plumb, I. C., and Ryan, K. R., "Kinetic Studies of the Reaction of C_2H_5 with O_2 at 295 K," Int. J. Chem. Kinet. 13, 1011 (1981)

Walker, R. W., "A Critical Survey of Rate Constants for Reactions in Gas-Phase Hydrocarbon Oxidation," in "Reaction Kinetics," A Specialist Report (The Chemical Society, Burlington House, London, 1975) Vol. 1 pg. 161

17,4 $C_2H_5 + H \rightarrow C_2H_6$ (a)

$\rightarrow CH_3 + CH_3$ (b)

$\rightarrow C_2H_4 + H_2$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Camilleri, et al. (1974)	503-753	$(1-3)x10^{17}$ Ar	$k_b = 6x10^{-11}$ $k_c = 3x10^{-12}$	2
Michael, et al. (1973)	300	$(2.5-15)x10^{16}$ He	$k_{a+b+c} = 3x10^{-11}$	2
Kurylo, et al. (1970)	298	$1.5x10^{18}$ He	$k_{a+b+c} = 6x10^{-11}$	1.5

Comments and Recommendations

Under the experimental conditions of the published work k(b) is the main reaction. We suggest the use of an overall rate of $6.0x10^{-11}cm^3molecule^{-1}s^{-1}$. The branching ratio for k_b/k_a for strong collisions can be found in Table A. Table B contains data on collision efficiencies. k_c is the rate constant for a disproportionation reaction. It should have no activation energy. For reaction in N_2 or polyatomics, on the basis of a step size down of 500 cm^{-1} and 1000 cm^{-1} respectively, we recommend:

$$\log(k_b/k_a(N_2,\ 0.1)) = -.98 + 2.641x10^{-3}T - 2.0x10^{-7}T^2$$
$$\log(k_b/k_a(N_2,\ 1)) = -1.915 + 2.69x10^{-3}T - 2.35x10^{-7}T^2$$
$$\log(k_b/k_a(N_2,\ 10)) = -2.975 + 3.048x10^{-3}T - 3.728x10^{-7}T^2$$

and

$$\log(k_b/k_a(C_2H_6,\ 0.1)) = -1.168 + 2.4275x10^{-3}T - 1.676x10^{-7}T^2$$
$$\log(k_b/k_a(C_2H_6,\ 1)) = -2.142 + 2.60x10^{-3}T - 2.44x10^{-7}T^2$$
$$\log(k_b/k_a(C_2H_6,\ 10)) = -3.263 + 3.061x10^{-3}T - 4.1136x10^{-7}T^2$$

We estimate the uncertainty as a factor of 3.

Table A. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K 300	 500	 700	 900	 1100	 1300	 1500	 1700	 1900	 2100	 2300	 2500
16.0	39	44	63	100	164	268	435	700	1102	1694	2540	3692
16.5	12	14	20.4	32.4	53	87	141	225	353	542	809	1176
17.0	3.9	4.6	6.8	11.0	18	29	47	75	116	177	262	379
17.5	1.3	1.6	2.4	4.0	6.5	10	16.6	26	40	60	88	125
18.0	0.42	0.56	0.91	1.5	2.5	4	6.3	9.7	14.6	21.4	31	43.3
18.5	0.14	0.19	0.35	0.62	1.04	1.7	2.6	3.9	5.7	8.2	11.5	15.1
19.0	0.044	0.066	0.13	0.24	0.43	0.7	1.1	1.7	2.4	3.3	4.6	6.21
19.5	0.013	0.02	0.04	0.09	0.17	0.29	0.47	0.71	1.03	1.4	1.95	2.56
20.0	0.004	0.007	0.015	0.03	0.06	0.11	0.19	0.30	0.44	0.61	0.82	1.07
20.5	0.001	0.002	0.005	0.01	0.02	0.04	0.07	0.11	0.17	0.25	0.34	0.44
21.0				0.003	0.007	0.01	0.02	0.04	0.06	0.09	0.13	0.17

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
300	0.15	0.31	0.52	0.70	0.83
500	0.072	0.18	0.35	0.56	0.73
700	0.040	0.11	0.25	0.44	0.64
900	0.024	0.07	0.18	0.35	0.56
1100	0.015	0.05	0.13	0.28	0.48
1300	0.010	0.033	0.096	0.22	0.41
1500	6.9×10^{-3}	0.024	0.071	0.18	0.35
1700	4.8×10^{-3}	0.017	0.053	0.14	0.30
1900	3.4×10^{-3}	0.012	0.039	0.11	0.25
2100	2.4×10^{-3}	8.6×10^{-3}	0.029	0.085	0.20
2300	1.7×10^{-3}	6.2×10^{-3}	0.021	0.066	0.17
2500	1.2×10^{-3}	4.5×10^{-3}	0.016	0.050	0.13

(W. Tsang, October 1984)

References

Camilleri, P., and Marshall, R. M., and Purnell, J. H., "Reaction of Hydrogen Atoms with Ethane," J. Chem. Soc., Faraday Trans. I 70, 1434 (1974)

Kurylo, M. J., Peterson, N. C., and Braun, W., "Absolute Rates of the Reactions H + C_2H_4 and H + C_2H_5," J. Chem. Phys. 53, 2776 (1970)

Michael, J. V., Osborne, D. T., and Suess, G. N., "Reaction H + C_2H_4: Investigation into the Effects of Pressure, Stoichiometry, and the Nature of the Third Body Species," J. Chem. Phys. 58, 2800 (1973)

17,5 $C_2H_5 + O \rightarrow CH_3CHO + H$ (a)

$\rightarrow HCHO + CH_3$ (b)

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Hoyermann, Sievert (1979)	300	$(0.64-3.2)\times10^{15}$ He	$k_a/k_b = 5 \pm 1$	

Comments and Recommendations

It is noteworthy that O does not abstract H from ethyl. In view of the well established rate constant of $1.6\times10^{-10}cm^3molecule^{-1}s^{-1}$ for the analogous CH_3 + O process, a similar value

should hold here. The product distribution suggests 1,2 hydrogen migration to be of considerable importance after addition. The uncertainty is a factor of 2.
(W. Tsang, May 1983)

References

Hoyermann, K., and Sievert, R., "The Reactions of Alkyl Radicals with Oxygen Atoms: Identification of Primary Products at Low Pressure," Symp. Combust. 17, (Combustion Institute, Pittsburgh, 1979) 517

17,6 $C_2H_5 + OH \rightarrow C_2H_4 + H_2O$ (a)
$\rightarrow CH_3 + H + HCHO$ (b)
$\rightarrow C_2H_5OH$ (c)

Comments and Recommendations

In the absence of experimental results it would appear that both abstraction as well as combination must be considered. Chemically activated ethanol can decompose to $C_2H_4 + H_2O$ as in (a) or via C-C bond cleavage to give products as in (b). Unfortunately there have been no determinations on the rate parameters for water elimination from ethanol. Thus the branching ratio for (a+b) and (c) is highly uncertain. At temperatures in excess 800 K and 1 atm N_2 we suggest using: $k_a = k_b = 4\times10^{-11}cm^3molecule^{-1}s^{-1}$
The estimated uncertainty is a factor of 4.
(W. Tsang, May 1983)

17,7 $C_2H_5 + HO_2 \rightarrow CH_3 + H_2CO + OH$ (a)
$\rightarrow C_2H_6 + O_2$ (b)
$\rightarrow C_2H_4 + H_2O_2$ (c)

Comments and Recommendations

There are no measurements on this system. We believe that addition will be considerabaly faster than abstraction and this will be followed by rapid decomposition of the adduct. The rate constant, k_a, can be expected to be close to the collisional value $\sim4\times10^{-11}cm^3molecule^{-1}s^{-1}$. Reaction (b) is estimated to have a rate constant of $5\times10^{-13}cm^3molecule^{-1}s^{-1}$ and is derived from the estimated rate for the reverse process. Reaction (c) is estimated to have a rate constant of $\sim5\times10^{-13}cm^3molecule^{-1}s^{-1}$ on the basis of disproportionation/combination ratios for normal alkyl radicals. The estimated uncertainties are a factor of 2.
(W. Tsang, May 1983)

17,8 $C_2H_5 + H_2O_2 \rightarrow C_2H_6 + HO_2$

$\log K_p = -1.61927 + 3236.63/T - 64487.6/T^2 + 4.5404\text{x}10^6/T^3$

Comments and Recommendations

In the absence of measurements we have calculated rate parameters on the basis of the rate of the reverse reaction and the equilibrium constant. This yields $k = 1.45\text{x}10^{-14}\exp(-490/T)$ $cm^3molecule^{-1}s^{-1}$. Here as in the methyl radical case, the small rate parameters lead one to suspect that the estimates used in determining the reverse rate expression are in error. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

17,9 $C_2H_5 + H_2O \rightarrow C_2H_6 + OH$

$\log K_p = -3.42 + 0.4 \log T - 4013/T$

Comments and Recommendations

In the absence of experimental data, we recommend the rate expression $k = 5.6\text{x}10^{-18}T^{1.44}\exp(-10150/T)cm^3molecule^{-1}s^{-1}$ on the basis of the recommendation for the rate of the reverse reaction $C_2H_6 + OH \rightarrow C_2H_5 + H_2O$ (see data sheet 11,6) and the equilibrium constant expression derived in Cohen and Westberg (1983). The uncertainty is a factor of 2.

(R. F. Hampson, May 1983)

References

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

17,10 $C_2H_5 + CH_4 \rightarrow C_2H_6 + CH_3$

$\log K_p = -.315613 - 1021.97/T + 5065/T^2 + .21958\text{x}10^7/T^3$

Comments and Recommendations

In the absence of experimental data, on the basis of the well established reverse rate [16,11] and the equilibrium constant we recommend

$k = 1.43\text{x}10^{-25}T^{4.14}\exp(-6322/T)cm^3molecule^{-1}s^{-1}$

The estimated uncertainty is a factor of 2 up to 1000 K.

(W. Tsang, May 1983)

17,12 $C_2H_5 + HCHO \rightarrow C_2H_6 + CHO$

Comments and Recommendations

Rate constants for reactions of alkyl radicals with aldehydic hydrogens are remarkably similar [J. A. Kerr and A. F. Trotman-Dickenson]. We recommend, in the absence of direct measurements, the rate espression for methyl radical attack on formaldehyde:

$$k(C_2H_5 + HCHO \rightarrow C_2H_6 + CHO) = 9.2x10^{-21}T^{2.81}exp(-2950/T)cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 2 up to 1000 K and a factor of 5 at 2500 K.

(W. Tsang, May 1983)

References

Kerr, J. A., and Trotman-Dickenson, A. F., "The Reactions of Alkyl Radicals," Progr. React. Kinet. Vol. 1 (Pergamon Press, New York, 1961) pg 105

17,14 $C_2H_5 + CO \rightarrow C_2H_5CO$

Reference	Conditions		Reaction rate constant,	Uncertainty
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Watkins, Thompson (1973)	238-378	$(3-75)x10^{17}$ CO, azoethane	$k\infty = 2.5x10^{-13}exp^{-1}/T)/s$	1.3

Comments and Recommendations

The rate constant expression of Watkins and Thompson should be used together with the fall-off corrections for strong colliders given in Table A. Collision efficiencies can be found in Table B. It should be noted that the weak C-CO bond for this system implies that under most conditions the reverse reaction is dominant. We estimate the uncertainty to be a factor of 2. Corrections for weak collisions for N_2 and for larger polyatomics (based on step size down of 500 cm^{-1} and 1000 cm^{-1} respectively) are as follows:

$$\log (k(poly, 0.1)/k\infty) = 0.299 - 7.589x10^{-4}T - 1.892x10^{-6}T^2$$
$$\log (k(poly, 1)/k\infty) = -0.181 + 1.38x10^{-3}T - 2.66x10^{-6}T^2$$
$$\log (k(poly, 10)/k\infty) = -0.53 + 2.469x10^{-3}T - 2.705x10^{-6}T^2$$

$$\log(k(N_2, 0.1)/k\infty) = 0.577 - 2.01x10^{-3}T - 1.495x10^{-6}T^2$$
$$\log(k(N_2, 1)/k\infty) = 0.093 + 4.62x10^{-4}T - 2.52x10^{-7}T^2$$
$$\log(k(N_2, 10)/k\infty) = 0.423 + 2.296x10^{-3}T - 3.0299x10^{-6}T^2$$

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.47	-1.89	-2.33	-2.77	-3.14	-3.45	-3.72	-3.93	-4.10	-4.23	-4.34	-4.43
17.0	-0.67	-1.02	-1.43	-1.83	-2.18	-2.47	-2.73	-2.93	-3.10	-3.23	-3.34	-3.43
18.0	-0.19	-0.41	-0.71	-1.01	-1.30	-1.54	-1.77	-1.96	-2.11	-2.24	-2.35	-2.44
19.0	-0.03	-0.10	-0.24	-0.41	-0.58	-0.74	-0.91	-1.05	-1.18	-1.29	-1.38	-1.46
20.0		-0.02	-0.05	-0.09	-0.15	-0.22	-0.30	-0.37	-0.44	-0.50	-0.56	-0.62
21.0			-0.01	-0.01	-0.02	-0.03	-0.05	-0.07	-0.08	-0.10	-0.12	-0.14

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.11	0.25	0.44	0.64	0.79
500	0.032	0.092	0.22	0.40	0.60
700	0.010	0.034	0.098	0.23	0.42
900	2.9×10^{-3}	0.011	0.035	0.098	0.23
1100	7.6×10^{-4}	2.7×10^{-3}	9.8×10^{-3}	0.033	0.093

(W. Tsang, October 1984)

References

Watkins, K. W., and Thompson, W. W., "Addition of Ethyl Radicals to Carbon Monoxide. Kinetic and Thermochemical Properties of the Propionyl Radical", Int. J. Chem. Kinet. 5, 791 (1973)

17,15 $C_2H_5 + HCO \rightarrow C_2H_6 + CO$ (a)

$\rightarrow C_2H_5CHO$ (b)

Comments and Recommendations

There are no measurements. We recommend values similar to those for the corresponding reactions of methyl radicals: $k(C_2H_5 + HCO \rightarrow C_2H_6 + CO) = 2 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ and $k(C_2H_5 + HCO \rightarrow C_2H_5CHO) = 3 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$. The uncertainty is a factor of 3. We have noted earlier that the disproportionation process for the methyl radical seems exceptionally fast.

(W. Tsang, May 1983)

17,16 $C_2H_5 + CH_3 \rightarrow C_3H_8$ (a)
$C_2H_5 + CH_3 \rightarrow CH_4 + C_2H_4$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Gibian, Corley (1972) review	298		$k_b/k_a \sim 0.04$	

Comments and Recommendations

There are no direct measurements. However, one can combine recombination rates for the reaction $2CH_3 \rightarrow C_2H_6$ and $2C_2H_5 \rightarrow C_4H_{10}$ which are well established over extended temperature ranges and through the combination to cross combination ratio determine $k_a\infty = 4.7x10^{-11}(300/T)^{0.5\pm0.5}cm^3molecule^{-1}s^{-1}$. The pressure dependence for strong colliders is given in Table A. Collision efficiencies as a function of downward step size and temperature can be found in Table B. The high temperature results for the reverse reaction indicate downward step sizes of about 400 cm^{-1} for argon and 600 cm^{-1} for Kr. We suggest the use of step sizes of 450 cm^{-1} for N_2 and 1000 cm^{-1} for larger polyatomics. This leads to the following correction factors at 0.1, 1, 10 atms, and at temperatures in excess of 900 K:

$$\log(k_a(N_2, 0.1)/k_a\infty) = -0.487 + 1.985x10^{-3}T - 1.874x10^{-6}T^2 + 2.121x10^{-10}T^3$$
$$\log(k_a(N_2, 1)/k_a\infty) = -0.3184 + 1.137x10^{-3}T - 8.353x10^{-7}T^2 - 2.156x10^{-11}T^3$$
$$\log(k_a(N_2, 10)/k_a\infty) = -9.683x10^{-2} + 2.233x10^{-4}T + 8.8824x10^{-8}T^2 - 2.0494x10^{-10}T^3$$

and

$$\log(k_a(C_3H_8, 0.1)/k_a\infty) = -0.357 + 1.347x10^{-3}T - 1.126x10^{-6}T^2 + 5.058x10^{-11}T^3$$
$$\log(k_a(C_3H_8, 1)/k_a\infty) =-0.213 + 6.91x10^{-4}T - 3.884x10^{-7}T^2 - 8.8893x10^{-11}T^3$$
$$\log(k_a(C_3H^8, 10)/k_a\infty) = 2.899x10^{-2} - 2.382x10^{-4}T + 4.771x10^{-7}T^2 - 2.557x10^{-10}T^3$$

The overall uncertainty is a factor of 2.

The disproportionation channel (b) has been studied by many workers. The rate expression is $k_b = .04\ k_a\infty$ with an uncertainty of 10%.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K 700	 900	 1100	 1300	 1500	 1700	 1900	 2100	 2300	 2500
16.0	-0.05	-0.17	-0.36	-0.62	-0.91	-1.22	-1.54	-1.85	-2.15	-2.43
16.5	-0.02	-0.09	-0.23	-0.43	-0.67	-0.94	-1.22	-1.50	-1.77	-2.02
17.0	-0.01	-0.05	-0.14	-0.28	-0.47	-0.69	-0.92	-1.17	-1.41	-1.64
17.5		-0.02	-0.07	-0.17	-0.30	-0.47	-0.66	-0.87	-1.08	-1.28
18.0		-0.01	-0.03	-0.09	-0.18	-0.30	-0.45	-0.61	-0.79	-0.95
18.5			-0.01	-0.04	-0.10	-0.18	-0.28	-0.40	-0.54	-0.67
19.0			-0.01	-0.02	-0.04	-0.09	-0.16	-0.24	-0.34	-0.43
19.5				-0.01	-0.02	-0.04	-0.08	-0.13	-0.19	-0.25
20.0					-0.01	-0.02	-0.03	-0.06	-0.09	-0.12
20.5						-0.01	-0.01	-0.02	-0.04	-0.05
21.0								-0.01	-0.01	-0.02

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.3	0.5	0.69	0.82
500	0.065	0.16	0.33	0.54	0.71
700	0.033	0.095	0.22	0.41	0.61
900	0.018	0.057	0.15	0.31	0.51
1100	0.01	0.035	0.09	0.23	0.42
1300	0.006	0.021	0.065	0.16	0.33
1500	0.0036	0.013	0.04	0.11	0.25
1700	0.0021	0.0078	0.026	0.078	0.19
1900	0.0012	0.0046	0.016	0.05	0.13
2100	0.0007	0.0026	0.0094	0.031	0.09
2300	0.00037	0.0012	0.0053	0.018	0.057
2500	0.00019	0.0075	0.0028	0.01	0.034

(W. Tsang, October 1984)

References

Gibian, M. J., and Corley, R. C., "Organic Radical-Radical Reactions Disproportionation vs Combination," Chem. Rev. 73, 443 (1973)

17,17 $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ (a)
$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6$ (b)

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}		
Parkes, Quinn (1976) review of pertinent literature together with modulation spectroscopy experiments	300-850		$k_a = 1.4x10^{-11}$	1.5
Kerr, Moss (1981) summary of over 30 experiments	300-673		$k_b/k_a = 0.13$	
Adachi, et al. (1979)	298	$1.5x10^{18}$ azoethane in propane	$k_a = 2x10^{-11}$ $k_{a+b} = 2.4x10^{-11}$	

Comments and Recommendations

We suggest the use of the rate expression $k_a = 1.8x10^{-11}$ and $k_b = 0.23x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of 30% over the temperature range 300-1000 K. The instability of C_2H_5 at higher temperature makes the small pressure dependence at high temperature and low pressure unimportant for practical purposes.

(W. Tsang, May 1984)

References

Adachi, H., Basco, N., and James, D. G. L., "A Quantitative Study of Alkyl Radical Reactions by Kinetic Spectroscopy. III. Absorption Spectrum and Rate Constants of Mutual Interaction for the Ethyl Radical," Int. J. Chem. Kinet. 11, 995 (1979)

Kerr, J. A., and Moss, S. J., "CRC Handbook of Bimolecular and Termolecular Reactions," CRC Press, Boca Raton, Florida Vol. II (1981) pg. 80

Parkes, D. A., and Quinn, C. P., "Study of the Spectra and Recombination Kinetics of Alkyl Radicals by Molecular Modulation Spectrometry. Part 2. The Recombination of Ethyl, Isopropyl and t-Butyl Radicals at Room Temperature and t-Butyl Radicals between 250 and 450 K," J. Chem. Soc., Faraday Trans. I 72, 1952 (1976)

18,1 $C_2H_4 \rightarrow C_2H_2 + H_2$ (a)
$\rightarrow C_2H_3 + H$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Kiefer, et al. (1983)	2300-3200	$(1-3)x10^{18}$ Kr	$k_a = 2.5x10^{-9}exp(-27900/T)$ $k_b = 2.3x10^{-9}exp(-41180/T)$	1.5
Tanzawa, Gardiner (1980)	2000-2500	$(1-3)x10^{18}$ Ar	$k_a = 4.9x10^{-7}exp(-40900/T)$ $k_b = 5x10^{-7}exp(-48140/T)$	2
Just, et al. (1977)	1700-2200	$(6-16)x10^{18}$	$k_a = 4.3x10^{-7}exp(-39900/T)$ $k_b = 6.3x10^{-7}exp(-49400/T)$	1.5

Comments and Recommendations

There is strong evidence that the main reaction in ethylene decomposition involves a molecular channel. Nevertheless, the sequence of reactions initiated by bond breaking will result in the same products. We have extrapolated the experimental data on the basis of RRKM calculations with the molecular process as the sole decomposition channel. Results are given in Table A for strong collisions. Weak collision effects are summarized in Table B. It is interesting to note that over the entire experimental range the reaction is in the intermediate pressure region.
The high pressure rate expression from 1100-2500 K: $k\infty = 10^{12.9}T^{0.44}exp(-44670/T)s^{-1}$ with an uncertainty of a factor of 3.
We have found that the experimental results are consistent with a down step size of 450 cm^{-1} for Argon and Krypton and this is probably also appropriate for N_2. For large polyatomics we suggest using a step size of 1000 cm^{-1}. On this basis the correction factors to the high pressure rate constants at 0.1, 1, and 10 atm and temperatures in excess of 1000 K for N_2(450 cm^{-1} step size down) and C_2H_4 (1000 cm^{-1} step size down) are as follows:

$$\log(k(N_2,0.1)/k\infty) = 1.044 - 1.174\times10^{-3}T - 1.016\times10^{-7}T^2$$
$$\log(k(N_2,\ 1)/k\infty) = 0.437 - 2.0917\times10^{-4}T - 2.6622\times10^{-7}T^2$$
$$\log(k(N_2,\ 10)/k\infty) = -0.162 + 5.156\times10^{-4}T - 3.514\times10^{-7}T^2$$

and

$$\log(k(\mathrm{poly},0.1)/k\infty) = 0.656 - 5.888\times10^{-4}T - 1.871\times10^{-7}T^2$$
$$\log(k(\mathrm{poly},\ 1)/k\infty) = 0.073 + 2.19643\times10^{-4}T - 3.035\times10^{-7}T^2$$
$$\log(k(\mathrm{poly},\ 10)/k\infty) = -0.32565 + 6.282\times10^{-4}T - 3.09822\times10^{-7}T^2$$

We estimate the uncertainties as a factor of 3.

With respect to the bond breaking reaction, we suggest the use of the experimentally determined expression of Just et al. or Tanzawa and Gardiner in the 1700-2500 K range with argon or N_2 as the third body. At the highest temperatures the expression of Kiefer is more appropriate.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K						
	1100	1300	1500	1700	1900	2100	2300
16.0	-0.68	-0.90	-1.11	-1.33	-1.54	-1.75	-1.96
16.5	-0.46	-0.64	-0.83	-1.02	-1.21	-1.40	-1.58
17.0	-0.29	-0.43	-0.59	-0.75	-0.91	-1.08	-1.24
17.5	-0.17	-0.27	-0.39	-0.52	-0.66	-0.80	-0.94
18.0	-0.09	-0.16	-0.24	-0.34	-0.45	-0.56	-0.68
18.5	-0.04	-0.08	-0.13	-0.20	-0.28	-0.37	-0.46
19.0	-0.02	-0.04	-0.07	-0.11	-0.16	-0.22	-0.28
19.5	-0.01	-0.01	-0.03	-0.05	-0.08	-0.12	-0.16
20.0		-0.01	-0.01	-0.02	-0.03	-0.05	-0.08
20.5				-0.01	-0.01	-0.02	-0.03
21.0						-0.01	-0.01

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
1100	0.017	0.053	0.14	0.30	0.50
1300	0.012	0.038	0.11	0.24	0.44
1500	8.4×10^{-3}	0.028	0.082	0.20	0.38
1700	6.1×10^{-3}	0.020	0.063	0.16	0.33
1900	4.5×10^{-3}	0.016	0.050	0.13	0.29
2100	3.4×10^{-3}	0.012	0.039	0.11	0.25
2300	2.5×10^{-3}	9.2×10^{-3}	0.031	0.084	0.21
2500	1.9×10^{-3}	7.1×10^{-3}	0.024	0.072	0.18

(W. Tsang, May 1983)

References

Just, Th., Roth, P., and Damm, R., "Production of Hydrogen Atoms During the Thermal Dissociation of Ethylene between 1700 and 2200 K," Symp. Combust. 16, (Combustion Institute, Pittsburgh, Pa., 1977) 961

Kiefer, J. H., Kapsalis,S. A., Al-Alami, M. Z., and Budach, K. A., "The Very High Temperature Pyrolysis of Ethylene and the Subsequent Reactions of Product Acetylene," Combust. Flame 51, 79 (1983)

Tanzawa, T., and Gardiner, W. C., Jr., "Thermal Decomposition of Ethylene," Combust Flame 39, 241 (1980)

18,2 $C_2H_4 + H_2 \rightarrow C_2H_5 + H$

$\log K_p = 0.74436 - 14858.89/T - 19924.0/T^2 + 0.58156 \times 10^7/T^3$

Comments and Recommendations

There are no experimental results on the rate of this reaction. However, on the basis of the rate of the reverse reaction $k(C_2H_5 + H \rightarrow C_2H_4 + H_2) = 3 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ [Camilleri, P., Marshall, R. M., and Purnell, H., "Reaction of Hydrogen Atoms with Ethane," J. Chem. Soc. Faraday Trans. I 70, 1434 (1974)] and the equilibrium constant we suggest $1.7 \times 10^{-11} \exp(-34300/T) cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 3.
(W. Tsang, May 1983)

18,3 $C_2H_4 + O_2 \rightarrow C_2H_3 + HO_2$

Comments and Recommendations

There are no measurements for the rate of this process. Following Walker's estimates for O_2 + alkane (Reaction Kinetics Vol I, (P. G. Ashmore, Sr. Reporter)), Chemical Society, London, 1974, pg. 161) we assign a rate expression for the abstraction process of $k = 7 \times 10^{-11} \exp(-29000/T) cm^3 molecule^{-1} s^{-1}$, with an uncertainty of a factor of 10. There is, however, the possibility of a lower lying channel involving addition and rearrangement prior to decomposition. Unfortunately we are not able to make any predictions for this process.
(W. Tsang, May 1983)

18,4 $C_2H_4 + H \rightarrow C_2H_5$ (a)

$\rightarrow C_2H_3 + H_2$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
(a) Lee, et al. (1978)	198-320	$\sim 1.5 \times 10^{19}$ Ar	$k_a^{\infty} = 3.67 \times 10^{-11} \exp(-1040/T)$	1.2
Mihelcic, et al. (1975)	300	$\sim 2.5 \times 10^{19}$ Ar	$k_a^{\infty} = 12.5 \times 10^{-13}$	1.3
Michael, et al. (1973)	300	6×10^{16} to 1.8×10^{19} He also H_2,N_2,Ar,Ne,Kr,SF_6	$k_a^{\infty} = 16.1 \times 10^{-13}$ also as f(P)	1.5
Kerr, Parsonage (1972) review	300-800		$k_a^{\infty} = 1.6 \times 10^{-10} \exp(-1410/T)$	
(b) Just, et al. (1977)	2000 1700	$(6-16) \times 10^{18}$ Ar	$k_b = 2.5 \times 10^{-11}$ $k_b = 0.8 \times 10^{-11}$	1.5

Comments and Recommendations

(a) There is good agreement for the value of this rate constant at 300 K. Combining this value with that for the reverse reaction at higher temperatures leads to

$$k(C_2H_4 + H \rightarrow C_2H_5) = 1.42 \times 10^{-15} T^{1.49} \exp(-499/T) cm^3 molecule^{-1} s^{-1}$$

with an uncertainty of a factor of 1.3.

Throughout most of this range the reaction is in the intermediate pressure region and the pressure dependence, in terms of logk/k∞ is given in Table A. Collision efficiencies as a function of downward step size and temperature can be found in Table B. The downward step sizes at room temperature are 80 cm^{-1} for H_2, 1000 cm^{-1} for SF_6, 300 cm^{-1} Kr, and 200 cm^{-1} for N_2, Ne and Ar. At higher temperatures the results for the reverse reaction yield a step size of 1000 cm^{-1} for ethane. Over the higher temperature (>600 K) range we suggest the use of a 450 cm^{-1} step size down for N_2. This leads to the following correction factors:

$$\log(k(N_2, 0.1)/k\infty) = 0.068 + 3.375 \times 10^{-4} T - 1.844 \times 10^{-6} T^2 + 3.65 \times 10^{-10} T^3$$

$$\log(k(N_2, 1)/k\infty) = -0.236 + 1.35 \times 10^{-3} T - 1.99 \times 10^{-6} T^2 + 3.44 \times 10^{-10} T^3$$

$$\log(k(N_2, 10)/k\infty) = -0.322 + 1.391 \times 10^{-3} T - 1.457 \times 10^{-6} T^2 + 1.881 \times 10^{-10} T^3$$

For larger polyatomics, a 1000 cm^{-1} step size down leads to the correction factors:

$$\log(k(poly, 0.1)/k\infty) = -0.051 + 6.73 \times 10^{-4} T - 1.707 \times 10^{-6} T^2 + 3.083 \times 10^{-10} T^3$$

$$\log(k(poly, 10)/k\infty) = 0.252 + 1.24 \times 10^{-3} T - 1.56 \times 10^{-6} T^2 + 2.33 \times 10^{-10} T^3$$

$$\log(k(poly, 10)/k\infty) = -0.228 + 9.11 \times 10^{-4} T - 8.32 \times 10^{-7} T^2 + 5.016 \times 10^{-11} T^3$$

The overall uncertainty is a factor of 2.

(b) The work of Just et al. is the only measurement of the rate constant for this reaction channel. We have fit a BEBO calibration to these data yielding $k_b = 2.2 \times 10^{-18} T^{2.53} \exp(-6160/T) cm^3 molecule^{-1} s^{-1}$

Table A. Values of $\log(k/k_\infty)$: dependence on concentration and temperature.

log[M]	T/K 300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.67	-0.84	-1.11	-1.45	-1.76	-2.07	-2.38	-2.66	-2.93	-3.18	-3.41	-3.62
16.5	-0.35	-0.51	-0.77	-1.06	-1.36	-1.66	-1.95	-2.22	-2.48	-2.72	-2.94	-3.14
17.0	-0.17	-0.29	-0.50	-0.75	-1.02	-1.29	-1.55	-1.81	-2.05	-2.27	-2.48	-2.68
17.5	-0.06	-0.15	-0.30	-0.51	-0.73	-0.96	-1.20	-1.42	-1.64	-1.85	-2.05	-2.23
18.0	-0.02	-0.07	-0.17	-0.31	-0.49	-0.68	-0.88	-1.07	-1.27	-1.45	-1.63	-1.80
18.5	-0.01	-0.03	-0.08	-0.18	-0.30	-0.44	-0.60	-0.76	-0.93	-1.09	-1.24	-1.39
19.0	-0.01	-0.01	-0.04	-0.09	-0.17	-0.27	-0.38	-0.51	-0.64	-0.77	-0.90	-1.02
19.5		-0.01	-0.01	-0.04	-0.08	-0.14	-0.21	-0.30	-0.40	-0.50	-0.60	-0.70
20.0				-0.01	-0.03	-0.07	-0.11	-0.16	-0.22	-0.30	-0.36	-0.44
20.5				-0.01	-0.01	-0.03	-0.05	-0.08	-0.11	-0.15	-0.19	-0.24
21.0						-0.01	-0.02	-0.03	-0.05	-0.07	-0.09	-0.11

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
300	0.14	0.30	0.50	0.69	0.82
500	0.063	0.16	0.33	0.53	0.71
700	0.031	0.091	0.22	0.40	0.60
900	0.017	0.053	0.14	0.30	0.50
1100	0.0097	0.032	0.09	0.22	0.40
1300	0.0056	0.020	0.06	0.16	0.32
1500	0.0033	0.012	0.038	0.11	0.24
1700	0.0019	0.007	0.024	0.07	0.18
1900	0.0011	0.004	0.015	0.047	0.13
2100	0.00065	0.0025	0.0089	0.030	0.087
2300	0.00036	0.0014	0.0052	0.018	0.057
2500	0.00021	0.0008	0.003	0.011	0.036

(W. Tsang, October 1984)

References

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18,5 $C_2H_4 + O \rightarrow CH_3 + HCO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Herron, Huie (1973)	200-500		$5.4x10^{-12}exp(-565/T)$	1.2
evaln.	298		$8.1x10^{-13}$	1.2
Peeters, Mahnen (1973)	1200-1700	$3x10^{17}$ O_2, 6.5-7.5% C_2H_4	$3.8x10^{-11}exp(-1360/T)$	
Atkinson, Pitts (1974)	300-392	$2x10^{18}$ Ar	$5.6x10^{-12}exp(-640/T)$	1.2
Singleton, Cvetanovic (1976)	298-486	$2x10^{18}$	$11.6x10^{-12}exp(-845/T)$	1.2
Atkinson, Pitts (1977)	298-439	$7x10^{17}$ Ar	$9.2x10^{-12}exp(-740/T)$	1.2
Nicovich, Ravishankara (1982)	298-940	$2x10^{18}$ Ar	$1.22x10^{-11}exp(-870/T)$ (Arrhenius expression given for 298-438 K)	1.2
Perry (1984)	294-820	$2x10^{18}$ Ar	$2.1x10^{-13}T^{0.63}exp(-690/T)$	1.2

Comments and Recommendations

The recommendation of Herron and Huie (1973) was based on the results reported by Davis et al. (1972) using the flash photolysis-resonance fluorescence technique over the temperature range 230-500 K, with additional room temperature determinations by flash photolysis-kinetic absorption spectroscopy and by discharge flow-mass spectrometry. The present recommendation is derived from a fit to those results, and those of Westenberg and deHaas (1969) for T<500 K, Atkinson and Pitts (1974), Singleton and Cvetanovic (1976), Atkinson and Pitts (1977), Nicovich and Ravishankara (1982) and Perry (1984).

The recommended rate expresion is $2.2x10^{-16}T^{1.55}exp(-215/T)cm^3molecule^{-1}s^{-1}$ over the range 230-940 K with an uncertainty of 20%.

Until recently, on the basis of final product analysis and also low pressure studies with mass spectrometric detection (Pruss et al. (1974), this reaction was thought to proceed by O atom addition followed by H atom migration in the complex and C-C bond breaking to give predominantly (95%) CH_3 + HCO with a minor channel to give $H_2C_2O + H_2$. However, recent experiments have shown that the vinoxy radical CH_2CHO is a major primary product of this reaction. Buss et al. (1981) in a crossed molecular beam study measured product angular and velocity distribution for all detectable mass peaks. They concluded that the major reaction channel proceeds by H atom elimination to give the vinoxy radical. The addition reaction channel to give CH_3 + HCO was determined to be unimportant in their system. Inoue and Akimoto (1981) have observed by laser induced fluorescence the vinoxy radical produced in this reaction. Kleinermanns and Luntz (1981) also observed this radical by laser induced fluorescence in a crossed molecular beam study of this reaction. Hunziker et al. (1981) studied this reaction in the 40-760 torr pressure range by a photochemical modulation

19,14 $C_2H_3 + CO \rightarrow C_2H_3CO$

Comments and Recommendations

There are no measurements on this reaction. We estimate the enthalpy of reaction to be 117 kJ mol^{-1}. The high pressure rate parameters should be close to that for ethyl + CO or $2.5\times10^{-13}\exp(-2420/T)cm^3molecule^{-1}s^{-1}$. The reaction is in the fall-off region under all conditions. The pressure dependence can be found in Table A. Collision efficiencies as a function of step size and temperature are summarized in Table B. Assuming a step size down of 450 cm^{-1} for N_2 and 1000 cm^{-1} for a polyatomic similar to C_2H_3CO we find the following correction factors at 0.1, 1, and 10 atm respectively:

$$\log(k(N_2, 0.1)/k\infty) = -0.129 + 1.07\times10^{-3}T - 2.099\times10^{-6}T^2 + 3.859\times10^{-10}T^3$$

$$\log(k(N_2, 1)/k\infty) = -0.34 + 1.5812\times10^{-3}T - 1.848\times10^{-6}T^2 + 2.785\times10^{-10}T^3$$

$$\log(k(N_2, 10)/k\infty) = -0.277 + 1.068\times10^{-3}T - 9.225\times10^{-7}T^2 + 4.606\times10^{-11}T^3$$

and

$$\log(k(poly, 0.1)/k\infty) = -0.190 + 1.136\times10^{-3}T - 1.784\times10^{-6}T^2 + 2.934\times10^{-10}T^3$$

$$\log(k(poly, 1)/k\infty) = -0.282 + 1.208\times10^{-3}T - 1.256\times10^{-6}T^2 + 1.371\times10^{-10}T^3$$

$$\log(k(poly, 10)/k\infty) = -0.14 + 4.757\times10^{-4}T - 2.829\times10^{-7}T^2 - 8.537\times10^{-11}T^3$$

The estimated uncertainty is a factor of 5.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.27	-0.5	-0.76	-1.06	-1.36	-1.63	-1.90	-2.15	-2.38	-2.59	-2.79	-2.96
16.5	-0.13	-0.28	-0.5	-0.75	-1.01	-1.26	-1.50	-1.73	-1.94	-2.14	-2.32	-2.50
17.0	-0.05	-0.15	-0.3	-0.50	-0.71	-0.92	-1.13	-1.33	-1.53	-1.71	-1.87	-2.02
17.5	-0.02	-0.07	-0.17	-0.3	-0.46	-0.63	-0.81	-0.98	-1.15	-1.30	-1.45	-1.59
18.0	-0.01	-0.03	-0.08	-0.16	-0.27	-0.39	-0.53	-0.67	-0.81	-0.94	-1.07	-1.19
18.5		-0.01	-0.03	-0.08	-0.14	-0.22	-0.32	-0.42	-0.52	-0.62	-0.72	-0.82
19.0			-0.01	-0.03	-0.06	-0.11	-0.17	-0.23	-0.30	-0.37	-0.44	-0.52
19.5				-0.01	-0.03	-0.05	-0.07	-0.11	-0.15	-0.19	-0.24	-0.29
20.0					-0.01	-0.02	-0.03	-0.04	-0.06	-0.09	-0.11	-0.13
20.5						-0.01	-0.01	-0.02	-0.02	-0.03	-0.04	-0.05
21.0								-0.01	-0.01	-0.01	-0.01	-0.02

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.29	0.49	0.68	0.82
500	0.059	0.15	0.32	0.52	0.70
700	0.029	0.084	0.20	0.38	0.59
900	0.0149	0.047	0.13	0.28	0.48
1100	$7.9x10^{-13}$	0.027	0.079	0.19	0.37
1300	$4.2x10^{-3}$	0.015	0.048	0.13	0.28
1500	$2.3x10^{-3}$	$8.4x10^{-3}$	0.028	0.083	0.20
1700	$1.2x10^{-3}$	$4.6x10^{-3}$	0.016	0.051	0.14
1900	$6.6x10^{-4}$	$2.5x10^{-3}$	$9.1x10^{-3}$	0.030	0.088
2100	$3.4x10^{-4}$	$1.3x10^{-3}$	$4.9x10^{-3}$	0.017	0.17
2300	$1.8x10^{-4}$	$6.9x10^{-4}$	$2.6x10^{-3}$	$9.5X10^{-3}$	0.031
2500	$8.9x10^{-4}$	$3.5x10^{-3}$	$1.35x10^{-3}$	$5.0x10^{-3}$	0.017

(W. Tsang, October 1984)

19,15 $C_2H_3 + HCO \rightarrow C_2H_4 + CO$ (a)
$\rightarrow C_2H_3CHO$ (b)

Comments and Recommendations

There are no rate measurements on these reactions. We suggest values similar to those for methyl + formyl interactions, $k_a = 1.5x10^{-10}cm^3molecule^{-1}s^{-1}$ and $k_b = 3x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3. Due to the small size of acrolein, k_b at higher temperatures will be in the fall off region thus further enhancing k_a. Uncertainty is a factor of 3.

(W. Tsang, May 1983)

is $C_2H_4 + HO_2 = C_2H_4OH_2^\dagger$ (1,-1), $C_2H_4OH^\dagger \rightarrow C_2H_4O + OH$ (2), where the rate constant is given by the expression $k = k_2k_1(k_2 + k_{-1})$. If we use $k_1 \sim 1\times10^{-12}\exp(-4000/T)\mathrm{cm^3molecule^{-1}s^{-1}}$ as appropriate for an addition reaction, then at 773 K, $k_2/k_{-1} \sim 1\times10^{-2}$. We suggest an expression of the form: $k = 1\times10^{-14}\exp(-4000/T)\mathrm{cm^3molecule^{-1}s^{-1}}$. If there is a pressure dependence then $C_2H_4O_2H^\dagger$ must be stabilized and this will represent an added complication. Obviously, much more data are needed. The estimated uncertainty is a factor of 3 at 773 K and much larger if long extrapolations are used.

(W. Tsang, May 1983)

References

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18,14 $C_2H_4 + CO \rightarrow C_2H_3 + HCO$

$\log K_p = 1.9929 - 19901.94/T + 115062/T^2 - 1.90896\times10^7/T^3$

Comments and Recommendations

There are no measurements on this system. On the basis of an assumed rate constant of $3.3\times10^{-12}\mathrm{cm^3molecule^{-1}s^{-1}}$ for the reverse reaction we find for the rate of the forward process, $k = 2.5\times10^{-10}\exp(-45600/T)\mathrm{cm^3molecule^{-1}s^{-1}}$, making it a very unlikely reaction under all combustion conditions. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

18,16 $C_2H_4 + CH_3 \rightarrow C_2H_3 + CH_4$ (a)
$\rightarrow nC_3H_7$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Kerr, Parsonage (1976) review	365-650		$k_a = 7\times10^{-13}\exp(-5590/T)$	
Kerr, Parsonage (1972) review	400-500		$k_b = 5.5\times10^{-13}\exp(-3877/T)$	1.3

Comments and Recommendations

Data on the second process are much more extensive than on the first. However at higher temperatures the important process will be (a). Our BEBO calculations match the results quite closely. A fit has been made by changing the activation barrier slightly. This leads to $k(CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3) = 1.1\times10^{-23}T^{3.7}\exp(-4780/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ with an uncertainty of a factor of 2. (W. Tsang, May 1984)

References

Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reaction of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds," (Butterworths, London, 1972)

Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals," (Butterworths, London, 1976)

18,17 $C_2H_4 + C_2H_5 \rightarrow C_2H_6 + C_2H_3$ (a)
$\rightarrow 1\text{-}C_4H_9$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
(a) Halstead, Quinn (1968)	798-924	$(1.1\text{-}17)\times10^{17}$ C_2H_4	$k_a = 6\times10^{-13}\exp(-8358/T)$	3
(b) Kerr, Parsonage (1972) review			$k_b = 2.5\times10^{-13}\exp(-3675/T)$	1.2

Comments and Recommendations

(a) The study by Halstead and Quinn is the only published report on the rate for this process. It is derived from studies on the pyrolysis of ethylene and depends on the interpretation of the mechanism. We have revised the expression from that published in order to reflect better established values for k(1-$C_4H_8 \rightarrow C_3H_5 + CH_3$) and k($2C_2H_5 \rightarrow C_4H_{10}$). A fit of the data has been made on the basis of BEBO calculations through a small variation in the activation barrier. This leads to $k_a = 1.05 \times 10^{-21} T^{3.13} \exp(-9063/T) cm^3 molecule^{-1} s^{-1}$. The estimated uncertainty is a factor of 10.

(b) It should be noted that in most combustion processes the reverse reaction will predominate over the radical combination.
(W. Tsang, May 1983)

References

Halstead, M. P., and Quinn, C. P., "Pyrolysis of Ethylene," Trans. Faraday Soc. 64, 103 (1968)

Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reaction of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds," (Butterworths, London, 1972)

18,18 $C_2H_4 + C_2H_4 \rightarrow C_2H_3 + C_2H_5$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
log K_p = 1.88585 - 15427.88/T - 156114/T^2 + 2.5437x10^7/T^3				
Boyd, et al. (1968)			$1 \times 10^{-9} \exp(-32200/T)$ (estimate based on reverse process)	
Ayranci, Back (1981)	700-773	$(1-6) \times 10^{18}$ C_2H_4	$2.4 \times 10^{-8} \exp(-33800/T)$	

Comments and Recommendations

Using the rate of the reverse process (19,17) and the equilibrium constant, we find $k(C_2H_4 + C_2H_4 \rightarrow C_2H_3 + C_2H_5) = 8 \times 10^{-10} \exp(-36000/T) cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 10. This expression is at wide variance with the observations of Ayranci and Back.
(W. Tsang, May 1984)

References

Ayranci, G., and Back, M. H., "Kinetics of the Bimolecular Initiation Process in the Thermal Reactions of Ethylene," Int. J. Chem. Kinet. 13, 897 (1981)

Boyd, M. L., Wu, T-M., and Back, M. H., "Kinetics of the Thermal Reactions of Ethylene. Part I," Can. J. Chem. 46, 2415 (1968)

19,1 $C_2H_3 + M \rightarrow C_2H_2 + H + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
log K_p = 5.777 - 8952.6/T + 94313.5/T^2				
Benson, Haugen (1967)	1300-1800	$2.8x10^{19}$	$1.3x10^{-9}exp(-15860/T)$	10
[Skinner, Sokoloski (1960)]	1100-1800	$2.8x10^{19}$ Ar 0.5-6% ethylene		

Comments and Recommendations

There are no direct measurements for this reaction. The work of Benson and Haugen is based on an analysis of the work of Skinner and Sokoloski. The determination of the rates of the reverse reaction is in the temperature range of 193 to 400 K. We have fit the results on the basis of RRKM calculations using these results as a basis. We find, on a strong collision basis, $k_o = 10^{7.88}(1/T)^{3.97}exp(-21712/T)cm^3molecule^{-1}s^{-1}$. The corrections for pressure effects can be found in Table A. Collision efficiency as a function of temperature and step size can be found in Table B. The parameters from Benson and Haugen suggest a down step size for argon of ~150 cm^{-1}. We believe a more appropriate step size down for N_2 is 450 cm^{-1} and 1000 cm^{-1} for polyatomics. This leads to the following rate expressions for T>600 K:

$k(N_2, 0) = 10^{17.84}T^{-7.49}exp(-22917/T)cm^3molecule^{-1}s^{-1}$

$log(k(N_2, 0.1)/k(N_2, 0)) = -1.689 + 2.889x10^{-3}T - 1.642x10^{-6}T^2 + 3.045x10^{-10}T^3$

$log(k(N_2, 1)/k(N_2, 0)) = -3.00 + 4.676x10^{-3}T - 2.511x10^{-6}T^2 + 4.497x10^{-10}T^3$

$log(k(N_2, 10)/k(N_2, 0)) = -4.347 + 5.991x10^{-3}T - 2.954x10^{-6}T^2 + 4.994x10^{-10}T^3$

and with C_2H_3 or similar polyatomics:

$k(C_2H_3, 0) = 10^{16.67}T^{-6.94}exp(-22863/T)cm^3molecule^{-1}s^{-1}$

$log(k(C_2H_3, 0.1)/k(C_2H_3, 0)) = -1.97 + 3.09x10^{-3}T - 1.671x10^{-6}T^2 + 3.01x10^{-10}T^3$

$log(k(C_2H_3, 1)/k(C_2H_3, 0)) = -3.277 + 4.636x10^{-3}T - 2.347x10^{-6}T^2 + 4.056x10^{-10}T^3$

$log(k(C_2H_3, 10)/k(C_2H_3, 0)) = -4.542 + 5.544x10^{-3}T - 2.505x10^{-6}T^2 + 3.99x10^{-10}T^3$

The rate constants are very much dependent on the uncertain thermochemistry for the vinyl radical. We estimate an uncertainty of a factor of 10 below 1000 K decreasing to a factor of 3 at 2500 K.

Table A. Values of $\log(k/k_\infty)$: dependence on concentration and temperature.

log[M]							T/K					
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.14	-0.10	-0.08	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.02	-0.02	-0.02
16.5	-0.28	-0.19	-0.16	-0.12	-0.10	-0.09	-0.08	-0.06	-0.06	-0.04	-0.04	-0.03
17.0	-0.48	-0.34	-0.27	-0.22	-0.18	-0.16	-0.14	-0.11	-0.10	-0.07	-0.07	-0.06
17.5	-0.76	-0.55	-0.44	-0.36	-0.30	-0.25	-0.22	-0.18	-0.16	-0.12	-0.11	-0.09
18.0	-1.15	-0.83	-0.64	-0.54	-0.45	-0.38	-0.32	-0.27	-0.23	-0.18	-0.16	-0.14
18.5	-1.67	-1.17	-0.94	-0.76	-0.64	-0.53	-0.46	-0.38	-0.33	-0.26	-0.23	-0.20
19.0	-2.13	-1.56	-1.26	-1.04	-0.87	-0.73	-0.63	-0.52	-0.46	-0.37	-0.33	-0.28
19.5	-2.61	-1.99	-1.64	-1.37	-1.14	-0.98	-0.85	-0.71	-0.62	-0.52	-0.46	-0.39
20.0	-3.10	-2.46	-2.07	-1.75	-1.47	-1.28	-1.12	-0.95	-0.83	-0.71	-0.63	-0.55
20.5	-3.60	-2.94	-2.53	-2.18	-1.88	-1.64	-1.42	-1.24	-1.10	-0.95	-0.85	-0.75
21.0	-4.10	-3.43	-3.02	-2.64	-2.30	-2.05	-1.80	-1.59	-1.42	-1.25	-1.12	-1.00

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K			Step-size (cm^{-1})		
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.69	0.83
500	0.069	0.17	0.35	0.55	0.72
700	0.037	0.10	0.24	0.43	0.63
900	0.022	0.066	0.17	0.34	0.54
1100	0.013	0.043	0.12	0.26	0.46
1300	8.5×10^{-3}	0.028	0.083	0.20	0.38
1500	5.6×10^{-3}	0.019	0.059	0.15	0.32
1700	3.7×10^{-3}	0.013	0.042	0.12	0.26
1900	2.5×10^{-3}	9×10^{-3}	0.03	0.087	0.21
2100	1.7×10^{-3}	6.2×10^{-3}	0.021	0.065	0.17
2300	1.2×10^{-3}	4.3×10^{-3}	0.015	0.048	0.12
2500	7.9×10^{-4}	3.0×10^{-3}	0.011	0.035	0.10

(W. Tsang, October 1984)

References

Benson, S. W., and Haugen, G. R., "Mechanisms for Some High-Temperature Gas-Phase Reactions of Ethylene, Acetylene, and Butadiene," J. Phys. Chem. 71, 1735 (1967)

Skinner, G. B., and Sokoloski, E., "Shock Tube Experiments on the Pyrolysis of Ethylene," J. Phys. Chem. 64, 1028 (1960)

19,2 $C_2H_3 + H_2 \rightarrow C_2H_4 + H$

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log $K_p = -1.14149 + 568.99/T + 136190/T^2 - 2.4092\times10^7/T^3$

Comments and Recommendations

There are no direct measurements for the rate of this process. From the equilibrium constant and the rate of the reverse reaction we derive $k = 5\times10^{-20}T^{2.63}\exp(-4298/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$. The uncertainty is a factor of 10.

(W. Tsang, May 1983)

19,3 $C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$ (a)
$\rightarrow C_2H_3O_2$ (b)

Comments and Recommendations

There are no measurements on the rates of these processes. By analogy with the reactions of ethyl radicals we estimate $k_a = 2\times10^{-13}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$ and $k_b = 1\times10^{-11}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$. Under combustion conditions the reverse of (b) predominates, making (a) the more important process. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

19,4 $C_2H_3 + H \rightarrow C_2H_2 + H_2$ (a)
$\rightarrow C_2H_4$ (b)

Comments and Recommendations

There are no experimental results on the rates of these processes. However, in view of the low lying molecular channel for ethylene decomposition (18,1) and on the basis of RRKM calculations it appears that the disproportionation channel (a) will be the most important with a rate constant in the region of $k(C_2H_3 + H \rightarrow C_2H_2 + H_2) = 1.6\times10^{-10}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$ with an uncertainty of a factor of 2.5.

(W. Tsang, May 1983)

19,5 $C_2H_3 + O \rightarrow CH_2CO + H$

Comments and Recommendations

There are no measurements on this process. On the basis of data on the reactions of methyl and ethyl radicals, rates can be expected to be fast $\simeq 1.6\times10^{-10}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$. The mechanism involves atom addition followed by adduct decomposition. Uncertainty is a factor of 3.

(W. Tsang, May 1983)

19,6 $C_2H_3 + OH \rightarrow H_2O + C_2H_2$ (a)
$\rightarrow CH_3CHO$ (b)

Comments and Recommendations

There are no measurements on the rate constants for these processes. They should both be close to collisional values ~ $5x10^{-11}cm^3molecule^{-1}s^{-1}$. Step (a) is an abstraction process, while step (b) involves combination followed by rearrangement. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

19,7 $C_2H_3 + HO_2 \rightarrow OH + CH_2CO + H$

Comments and Recommendations

In the absence of experimental data and since the competing abstraction reaction should be quite slow in comparison to additon, we postulate the reaction to proceed by an addition mechanism with rapid decomposition of the hot adduct. The overall rate constant can be expected to have a near collisional value ~ $5x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, May 1983)

19,8 $C_2H_3 + H_2O_2 \rightarrow C_2H_4 + HO_2$

Comments and Recommendations

In the absence of experimental results we estimate this rate constant to be similar to that for the methyl abstraction reaction ~$2x10^{-14}exp(300/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 10.

(W. Tsang, May 1983)

19,9 $C_2H_3 + H_2O \rightarrow C_2H_4 + OH$

Comments and Recommendations

There are no reported measurements on this reaction. We suggest the use of a rate expression similar to that for methyl radical attack on water, $k(C_2H_3 + H_2O \rightarrow C_2H_4 + OH) = 8x10^{-22}T^{2.9}exp(-7480/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 5 at temperatures above 1000 K and larger at lower temperatures.

(W. Tsang, May 1983)

19,10 $C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3$

$\log K_p = 0.36863 + 381.89/T + 102549/T^2 - 1.2471\times10^7/T^3$

Comments and Recommendations

There are no reported measurements on the rate of this process. We have used the rate expression for the reverse reaction and the equilibrium constant to determine the rate expression $k(C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3) = 2.4\times10^{-24}T^{4.02}\exp(-2754/T)\mathrm{cm^3molecule^{-1}s^{-1}}$. The uncertainty is a factor of 5 at temperatures in excess of 1000 K and larger at lower temperatures.

(W. Tsang, May 1983)

19,11 $C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5$

$\log K_p = 0.68488 + 1403.86/T + 97484/T^2 - 1.46668\times10^7/T^3$

Comments and Recommendations

In the absence of experimental results we have utilized the rate of the reverse reaction [18,17] and the equilibrium constant to yield $k(C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5) = 10^{-21}T^{3.3}\exp(-5285/T)\mathrm{cm^3molecule^{-1}s^{-1}}$. The uncertainty is a factor of 5 at temperatures in excess of 1000 K and larger at lower temperatures.

(W. Tsang, May 1983)

19,12 $C_2H_3 + H_2CO \rightarrow C_2H_4 + HCO$

Comments and Recommendations

In the absence of any direct measurements, we make use of the rate expression for methyl abstraction (16,12) and note the similarities of the rates of abstraction of aldehydic hydrogen by alkyl radicals. (J. A. Kerr and A. F. Trotman-Dickenson, Progr. React. Kinet., Vol. 1, G. Porter and B. Stevens, ed., Pergamon Press, New York, 1961). This leads to the rate expression $9\times10^{-21}T^{2.81}\exp(-2950/T)\mathrm{cm^3molecule^{-1}s^{-1}}$. The uncertainty is a factor of 5 at temperatures in excess of 1000 K and larger at lower temperatures.

(W. Tsang, May 1983)

19,14 $C_2H_3 + CO \rightarrow C_2H_3CO$

Comments and Recommendations

There are no measurements on this reaction. We estimate the enthalpy of reaction to be 117 kJ mol^{-1}. The high pressure rate parameters should be close to that for ethyl + CO or $2.5x10^{-13}exp(-2420/T)cm^3molecule^{-1}s^{-1}$. The reaction is in the fall-off region under all conditions. The pressure dependence can be found in Table A. Collision efficiencies as a function of step size and temperature are summarized in Table B. Assuming a step size down of 450 cm^{-1} for N_2 and 1000 cm^{-1} for a polyatomic similar to C_2H_3CO we find the following correction factors at 0.1, 1, and 10 atm respectively:

$$\log(k(N_2,\ 0.1)/k\infty) = -0.129 + 1.07x10^{-3}T - 2.099x10^{-6}T^2 + 3.859x10^{-10}T^3$$

$$\log(k(N_2,\ 1)/k\infty) = -0.34 + 1.5812x10^{-3}T - 1.848x10^{-6}T^2 + 2.785x10^{-10}T^3$$

$$\log(k(N_2,\ 10)/k\infty) = -0.277 + 1.068x10^{-3}T - 9.225x10^{-7}T^2 + 4.606x10^{-11}T^3$$

and

$$\log(k(poly,\ 0.1)/k\infty) = -0.190 + 1.136x10^{-3}T - 1.784x10^{-6}T^2 + 2.934x10^{-10}T^3$$

$$\log(k(poly,\ 1)/k\infty) = -0.282 + 1.208x10^{-3}T - 1.256x10^{-6}T^2 + 1.371x10^{-10}T^3$$

$$\log(k(poly,\ 10)/k\infty) = -0.14 + 4.757x10^{-4}T - 2.829x10^{-7}T^2 - 8.537x10^{-11}T^3$$

The estimated uncertainty is a factor of 5.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.27	-0.5	-0.76	-1.06	-1.36	-1.63	-1.90	-2.15	-2.38	-2.59	-2.79	-2.96
16.5	-0.13	-0.28	-0.5	-0.75	-1.01	-1.26	-1.50	-1.73	-1.94	-2.14	-2.32	-2.50
17.0	-0.05	-0.15	-0.3	-0.50	-0.71	-0.92	-1.13	-1.33	-1.53	-1.71	-1.87	-2.02
17.5	-0.02	-0.07	-0.17	-0.3	-0.46	-0.63	-0.81	-0.98	-1.15	-1.30	-1.45	-1.59
18.0	-0.01	-0.03	-0.08	-0.16	-0.27	-0.39	-0.53	-0.67	-0.81	-0.94	-1.07	-1.19
18.5		-0.01	-0.03	-0.08	-0.14	-0.22	-0.32	-0.42	-0.52	-0.62	-0.72	-0.82
19.0			-0.01	-0.03	-0.06	-0.11	-0.17	-0.23	-0.30	-0.37	-0.44	-0.52
19.5				-0.01	-0.03	-0.05	-0.07	-0.11	-0.15	-0.19	-0.24	-0.29
20.0					-0.01	-0.02	-0.03	-0.04	-0.06	-0.09	-0.11	-0.13
20.5						-0.01	-0.01	-0.02	-0.02	-0.03	-0.04	-0.05
21.0								-0.01	-0.01	-0.01	-0.01	-0.02

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.29	0.49	0.68	0.82
500	0.059	0.15	0.32	0.52	0.70
700	0.029	0.084	0.20	0.38	0.59
900	0.0149	0.047	0.13	0.28	0.48
1100	7.9×10^{-13}	0.027	0.079	0.19	0.37
1300	4.2×10^{-3}	0.015	0.048	0.13	0.28
1500	2.3×10^{-3}	8.4×10^{-3}	0.028	0.083	0.20
1700	1.2×10^{-3}	4.6×10^{-3}	0.016	0.051	0.14
1900	6.6×10^{-4}	2.5×10^{-3}	9.1×10^{-3}	0.030	0.088
2100	3.4×10^{-4}	1.3×10^{-3}	4.9×10^{-3}	0.017	0.17
2300	1.8×10^{-4}	6.9×10^{-4}	2.6×10^{-3}	9.5×10^{-3}	0.031
2500	8.9×10^{-4}	3.5×10^{-3}	1.35×10^{-3}	5.0×10^{-3}	0.017

(W. Tsang, October 1984)

19,15 $C_2H_3 + HCO \rightarrow C_2H_4 + CO$ (a)
$\rightarrow C_2H_3CHO$ (b)

Comments and Recommendations

There are no rate measurements on these reactions. We suggest values similar to those for methyl + formyl interactions, $k_a = 1.5\times10^{-10}\,cm^3 molecule^{-1}s^{-1}$ and $k_b = 3\times10^{-11}\,cm^3 molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3. Due to the small size of acrolein, k_b at higher temperatures will be in the fall off region thus further enhancing k_a. Uncertainty is a factor of 3.

(W. Tsang, May 1983)

19,16 $C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4$ (a)
$\rightarrow C_3H_5 + H$ (b)
$\rightarrow C_3H_6$ (c)

Comments and Recommendations

There are no direct measurements on these processes. We assume that the disproportionation/combination ratio will be similar to that for $CH_3 + C_2H_5$. This leads to $k_a = 6.5\times10^{-13} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 3. The results for combination and the chemically activated decomposition are summarized in Tables A and B with $k_{b+c}(\infty) = 4.2\times10^{-11} cm^3 molecule^{-1} s^{-1}$. Collision efficiency as a function of temperature and step size can be found in Table C. We suggest using a down step size of 450 cm^{-1} for N_2, O_2, Ar and 1000 cm^{-1} for larger polyatomics. Uncertainties are a factor of 3. As can be seen in Table A, the pressure dependence for k_{b+c} is small. We recommend at 1 atm and with a polyatomic third body the correction factor:

$$\log(k_{b+c}(\text{poly}, 1)/k_{b+c}\infty) = -0.177 + 6.687\times10^{-4}T - 6.040\times10^{-7}T^2 + 1.07234\times10^{-10}T^3$$

Within a factor of 1.5, it is also applicable for 0.1 and 10 atm and for N_2 at 0.1, 1, and 10 atm The branching ratio is strongly pressure dependent. The decomposition (b) to stablization (c) ratios for N_2 and polyatomics at 0.1, 1 and 10 atm are:

$$\log(k_b/k_c(N_2, 0.1)) = 10^{-27.77}T^{8.66}\exp(1639/T)$$
$$\log(k_b/k_c(N_2, 1)) = 10^{-27.95}T^{8.52}\exp(1248/T)$$
$$\log(k_b/k_c(N_2, 10)) = 10^{-30.76}T^{9.16}\exp(1379.3/T)$$

and

$$\log(k_b/k_c(\text{poly}, 0.1)) = 10^{-26.25}T^{8.07}\exp(1336.5/T)$$
$$\log(k_b/k_c(\text{poly}, 1)) = 10^{-28.07}T^{8.42}\exp(1268/T)$$
$$\log(k_b/k_c(\text{poly}, 10)) = 10^{-32.09}T^{9.41}\exp(1650/T)$$

Uncertainties are a factor of 5

Table A. Values of $\log(k_{b+c}/k_{b+c}\infty)$: dependence on concentration and temperature.

log[M]	T/K									
	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.17	-0.28	-0.38	-0.47	-0.53	-0.57	-0.60	-0.61	-0.61
16.5	-0.04	-0.11	-0.20	-0.29	-0.39	-0.47	-0.53	-0.57	-0.59	-0.60
17.0	-0.02	-0.06	-0.12	-0.21	-0.30	-0.38	-0.46	-0.51	-0.55	-0.57
17.5	-0.01	-0.03	-0.07	-0.12	-0.20	-0.29	-0.37	-0.43	-0.49	-0.52
18.0		-0.01	-0.03	-0.07	-0.12	-0.19	-0.27	-0.33	-0.39	-0.44
18.5			-0.01	-0.03	-0.07	-0.11	-0.17	-0.23	-0.30	-0.35
19.0				-0.01	-0.03	-0.06	-0.10	-0.14	-0.19	-0.24
19.5					-0.01	-0.03	-0.05	-0.07	-0.10	-0.14
20.0						-0.01	-0.02	-0.03	-0.05	-0.07
20.5							-0.01	-0.02	-0.02	-0.03
21.0								-0.01	-0.01	-0.02

Table B. Values of branching ratio k(decomp)/k(stabl): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	0.006	0.02	0.12	0.28	0.56	1.04	1.89	3.41	6.12	10.91	19.3	33.5
16.5	0.002	0.008	0.052	0.13	0.27	0.50	0.90	1.56	2.73	4.7	8.0	13.3
17.0		0.003	0.02	0.056	0.12	0.24	0.44	0.76	1.28	2.1	3.5	5.7
17.5			0.007	0.023	0.056	0.12	0.21	0.37	0.62	1.0	1.62	2.5
18.0				0.009	0.024	0.05	0.10	0.18	0.31	0.50	0.78	1.18
18.5				0.0017	0.009	0.02	0.048	0.089	0.15	0.25	0.38	0.57
19.0					0.002	0.009	0.021	0.041	0.07	0.12	0.184	0.27
19.5							0.008	0.017	0.03	0.054	0.086	0.13
20.0								0.004	0.013	0.023	0.034	0.056
20.5								0.0014	0.003	0.0087	0.014	0.022
21.0									0.001	0.002	0.003	0.015

Table C. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.29	0.49	0.68	0.82
500	0.065	0.17	0.33	0.54	0.72
700	0.036	0.10	0.24	0.43	0.62
900	0.022	0.060	0.17	0.34	0.54
1100	0.013	0.043	0.12	0.26	0.46
1300	8.7×10^{-3}	0.029	0.084	0.20	0.39
1500	5.7×10^{-3}	0.020	0.061	0.16	0.32
1700	3.8×10^{-3}	0.013	0.043	0.12	0.26
1900	2.5×10^{-3}	9.2×10^{-3}	0.031	0.088	0.21
2100	1.7×10^{-3}	6.3×10^{-3}	0.022	0.066	0.17
2300	1.1×10^{-3}	4.3×10^{-3}	0.015	0.048	0.13
2500	7.5×10^{-4}	2.9×10^{-3}	0.010	0.034	0.097

(W. Tsang, October 1984)

19,17 $C_2H_3 + C_2H_5 \rightarrow 1\text{-}C_4H_8$ (a)

$\rightarrow C_3H_5 + CH_3$ (b)

$\rightarrow C_2H_4 + C_2H_4$ (c)

$\rightarrow C_2H_2 + C_2H_6$ (d)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Ibuki, Takezaki (1975)	298	$2.3x10^{19}$ H_2	k_c/k_a =0.68 k_d/k_a =0.37	
James, Troughton (1966)	434-448	$9x10_{17}$ 1.1 mixture diethyl ketone diallyl	k_d/k_a =0.12 k_c/k_a =0.034	

Comments and Recommendations

The measurements on the disproportionation to combination ratios are discordant. We favor the lower numbers mainly due to the similarity to that for ethyl disproportionation and combination. Therefore, $k_d=k_c$ = $0.8x10^{-12}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3. The main reaction is recombination, k_{a+b} = $2.5x10^{-11}cm^3molecule^{-1}s^{-1}$, where (b) is the decomposition pathway for chemically activated 1-butene with almost no pressure dependence. The branching ratios are given in Table A. Collision efficiencies as a function of step size can be found in Table B. Decomposition to stabilization ratios with nitrogen (450 cm^{-1} step size down) and a polyatomic molecule similar to 1-butene (1000 cm^{-1} step size down) at 0.1, 1 and 10 atm are as follows:

$$\log(k_b/k_a(N_2,\ 0.1)) = 10^{-37.6}T^{12.08}\exp(3946/T)$$
$$\log(k_b/k_a(N_2,\ 1)) = 10^{-35.6}T^{11.25}\exp(3289/T)$$
$$\log(k_b/k_a(N_2,\ 10)) = 10^{-35.03}T^{10.83}\exp(2853/T)$$
$$\log(k_b/k_a(\text{poly},\ 0.1)) = 10^{-19.7}T^{6.7}\exp(25.7/T)$$
$$\log(k_b/k_a(\text{poly},\ 1)) = 10^{-19.0}T^{6.11}\exp(23.70/T)$$
$$\log(k_b/k_a(\text{poly},\ 10)) = 10^{-20.96}T^{6.49}\exp(25.15/T)$$

Uncertainties are a factor of 5.

Table A. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	0.70	1.14	2.42	5.10	10.3	20.8	41.5	81.4	155	281	476	745.9
16.5	0.23	0.42	0.96	2.04	4.05	7.9	15.3	29.1	53.7	95	158	244
17.0	0.08	0.15	0.38	0.85	1.69	3.26	6.1	11.2	19.8	34	54.7	82.4
17.5	0.024	0.05	0.15	0.35	0.73	1.42	2.61	4.6	7.9	13.9	20.0	29.2
18.0	0.008	0.017	0.05	0.14	0.31	0.63	1.16	2.0	3.32	5.2	7.79	10.9
18.5	0.002	0.006	0.018	0.05	0.12	0.27	0.51	0.90	1.46	2.2	3.2	4.3
19.0		0.002	0.006	0.018	0.05	0.11	0.22	0.39	0.64	0.96	1.35	1.76
19.5			0.002	0.005	0.016	0.04	0.09	0.16	0.27	0.41	0.56	0.72
20.0				0.002	0.005	0.014	0.03	0.06	0.11	0.16	0.22	0.28
20.5					0.002	0.004	0.01	0.02	0.04	0.058	0.08	0.098
21.0						0.001	0.003	0.007	0.01	0.019	0.026	0.033

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.30	0.50	0.69	0.82
500	0.064	0.16	0.33	0.53	0.71
700	0.033	0.094	0.22	0.41	0.61
900	0.018	0.056	0.15	0.31	0.51
1100	0.01	0.034	0.097	0.23	0.41
1300	5.9×10^{-3}	0.020	0.062	0.16	0.32
1500	3.5×10^{-3}	0.012	0.040	0.11	0.25
1700	2.0×10^{-3}	7.3×10^{-3}	0.025	0.074	0.18
1900	1.1×10^{-3}	4.2×10^{-3}	0.015	0.048	0.13
2100	6.2×10^{-4}	2.4×10^{-3}	8.6×10^{-3}	0.029	0.084
2300	3.3×10^{-4}	1.3×10^{-3}	4.7×10^{-3}	0.016	0.051
2500	1.6×10^{-4}	6.4×10^{-4}	2.4×10^{-3}	8.8×10^{-3}	0.029

(W. Tsang, October 1984)

References

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James, D. G., and Troughton, G. E., "Reactions of Allylic Radicals," Trans. Faraday Soc. 62, 145 (1966)

19,18 $C_2H_3 + C_2H_4 \rightarrow C_4H_6 + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Benson, Haugen (1967)	1100-1800	2.8×10^{19} Ar 0.5-6% ethylene in argon	$8.3 \times 10^{-13}\exp(-3676/T)$	10

Comments and Recommendations

This expression is based on Benson and Haugen's analysis of the results of Skinner and Sokoloski. The reaction proceeds through the formation of an adduct which rapidly decomposes. The rate parameters are in the range expected for addition reactions and as written the expression is suitable for most high temperature purposes. The uncertainty is a factor of 10.

(W. Tsang, May 1984)

References

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19,19 $C_2H_3 + C_2H_3 \rightarrow C_4H_6$ (a)
$\rightarrow C_2H_2 + C_2H_4$ (b)
$\rightarrow C_4H_5 + H$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
MacFadden, Currie (1973)	298	5×10^{15} divinylether, acetylene, ethylene, CO	$k_b = 5 \times 10^{-12}$	
Sherwood, Gunning (1965)	323	1×10^{17} divinylmercury	$k_b/k_a = 0.02$	
Weir (1965)	448	1×10^{18} acryaldehyde, vinyl formate	$k_b/k_a = 1.0$	
Ibuki, Takezaki (1975)	298	2.3×10^{19} He	$k_b/k_a = 0.087$	

Comments and Recommendations

There is very little definitive information on these reactions. We suggest that recombination of vinyl will be very much like that of ethyl with a high pressure rate of $k_{a+c} = 1.6 \times 10^{-11} cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3. The disproportionation rate is estimated to be $1.6\times10^{-12}\mathrm{cm^3molecule^{-1}s^{-1}}$. The results of McFadden and Currie are affected by uncertainties in reaction conditions while those of Sherwood and Gunning and Weir suffer from complexities in the reaction mechanism. The possibility of an exothermic decomposition channel (c) represents an added complication. Results of RRKM calculations on the assumption of strong collisions can be found in Tables A and B. Weak collision effects can be found in Table C. We suggest the use of a down step size of 450 $\mathrm{cm^{-1}}$ for N_2 and Argon and 1000 $\mathrm{cm^{-1}}$ for large polyatomics. This leads to the following expression:

$$\log(k_{a+c}/k_{a+c}\infty) = -0.040 + 1.044\times10^{-4}T - 5.419\times10^{-9}T^2 - 5.068\times10^{-11}T^3$$

At 1 atm for butadiene this is within a factor of 1.6 of all other results in N_2 and C_4H_6.

Branching ratios are:

$\log(k_c/k_a(N_2,\ 0.1)) = 10^{-24.6}T^{7.56}\exp(1310/T)$
$\log(k_c/k_a(N_2,\ 1)) = 10^{-26.9}T^{8.07}\exp(1315/T)$
$\log(k_c/k_a(N_2,\ 10)) = 10^{-31.3}T^{9.1}\exp(1767/T)$
$\log(k_c/k_a(C_4H_6,\ 0.1)) = 10^{-24.3}T^{7.36}\exp(1247.7/T)$
$\log(k_c/k_a(C_4H_6,\ 1)) = 10^{-28.2}T^{8.33}\exp(1565.8/T)$
$\log(k_c/k_a(C_4H_6,\ 10)) = 10^{-33.3}T^{9.63}\exp(2176.5/T)$

Uncertainty in the rate of vinyl disappearance (k_a+k_c) is a factor of 3, while that for the branching ratio is a factor of 10.

Table A. Values of $\log(k_{a+c}/k_{a+c}\infty)$: dependence on concentration and temperature.

log[M]	T/K									
	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.01	-0.02	-0.07	-0.13	-0.22	-0.31	-0.41	-0.51	-0.58	-0.65
16.5		-0.01	-0.04	-0.09	-0.17	-0.25	-0.34	-0.43	-0.52	-0.60
17.0			-0.02	-0.04	-0.10	-0.18	-0.26	-0.35	-0.44	-0.52
17.5			-0.01	-0.02	-0.06	-0.11	-0.18	-0.25	-0.32	-0.42
18.0				-0.01	-0.03	-0.06	-0.11	-0.16	-0.22	-0.30
18.5					-0.01	-0.03	-0.06	-0.10	-0.14	-0.20
19.0						-0.01	-0.03	-0.05	-0.07	-0.11
19.5							-0.01	-0.02	-0.03	-0.05
20.0								-0.01	-0.01	-0.02
20.5										-0.01

Table B. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K 300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	0.013	0.025	0.07	0.15	0.28	0.47	0.76	1.17	1.78	2.7	4.1	6
16.5		0.01	0.026	0.065	0.13	0.23	0.39	0.60	0.90	1.3	1.9	2.7
17.0			0.01	0.026	0.06	0.11	0.20	0.31	0.47	0.68	0.95	1.3
17.5				0.01	0.025	0.05	0.10	0.16	0.24	0.35	0.48	0.64
18.0					0.009	0.02	0.045	0.08	0.12	0.18	0.24	0.32
18.5						0.007	0.019	0.035	0.058	0.086	0.12	0.16
19.0							0.01	0.015	0.025	0.039	0.055	0.07
19.5									0.01	0.016	0.023	0.03
20.0											0.01	0.01

Table C. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
300	0.15	0.31	0.51	0.69	0.83
500	0.069	0.17	0.35	0.55	0.72
700	0.037	0.10	0.24	0.43	0.63
900	0.021	0.066	0.17	0.34	0.54
1100	0.014	0.043	0.12	0.26	0.46
1300	$8.5x10^{-3}$	0.028	0.083	0.20	0.38
1500	$5.5x10^{-3}$	0.019	0.058	0.15	0.32
1700	$3.6x10^{-3}$	0.013	0.041	0.11	0.26
1900	$2.4x10^{-3}$	0.0086	0.029	0.084	0.20
2100	$1.6x10^{-3}$	0.0057	0.020	0.061	0.16
2300	$1.0x10^{-3}$	0.0038	0.014	0.043	0.12
2500	$6.5x10^{-4}$	0.0025	$9.0x10^{-3}$	0.030	0.087

(W. Tsang, October 1984)

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Sherwood, A. G., and Gunning, H. E., "The Photolysis of Mercury Divinyl," J. Phys. Chem. 69, 2323 (1965)

Weir, N. A., "Preparation and Reactions of Vinyl Radicals," J. Chem. Soc., 6870 (1965)

20,1 $C_2H_2 \rightarrow C_2H + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Tanzawa, Gardiner (1979)	1700-3400	$(6-18)x10^{17}$ 1-10% C_2H_2 in Ar	$7x10^{-8}exp(-53800/T)$	
Frank, Just (1980)	2100-3000	$(3.6-16)x10^{18}$ 5-400 ppm C_2H_2 in Ar	$(6\pm1)x10^{-8}exp(-53600/T)$	

Comments and Recommendations

The experimental results are in excellent agreement. Both are from shock tube experiments but with different analytical methodology; Frank and Just used resonance absorption with H atom detection and Tanzawa and Gardiner used a variety of methods. At the high temperatures the rates are clearly in the bimolecular region. We have carried out RRKM calculation with a high pressure recombination rate ~$3x10^{-10}cm^3molecule^{-1}s^{-1}$ and confirm Frank and Just's conclusion that for argon in this temperature range the collision efficiency is 0.02. On this basis, one would have expected somewhat greater divergence between the two reported rate expressions. We recommend, on a strong collision basis, $k_o = 10^{9.4}T^{-3.7}exp(-63985/T)cm^3molecule^{-1}s^{-1}$. The departure from a bimolecular process is summarized in Table A. For argon as a third body we find β_c commensurate with a downward step size of 300 cm^{-1}. Since there are no data for other third bodies we suggest using 1000 cm^{-1} for larger polyatomics. Table B give β_c as a function of step size and temperature. The high pressure rate expression is $k\infty = 10^{15.42}exp(-62445/T)s^{-1}$. With N_2 as the weak collider and a step size down of 300 cm^{-1} we find:

$$\log(k(N_2,\ 0.1)/k\infty) = 0.347 - 1.228x10^{-3}T + 3.435x10^{-8}T^2$$
$$\log(k(N_2,\ 1)/k\infty) = 0.178 - 3.966x10^{-4}T - 1.338x10^{-7}T^2$$
$$\log(k(N_2,\ 10)/k\infty) = 0.005 + 7.854x10^{-5}T - 1.775x10^{-7}T^2$$

For C_2H_2 and with a step size down of 1000 cm^{-1} correction factors are:

$$\log(k(C_2H_2,\ 0.1)/k\infty) = 0.476 - 2.015x10^{-3}T + 1.908x10^{-7}T^2$$
$$\log(k(C_2H_2,\ 1)/k\infty) = 0.372 - 1.0081x10^{-3}T - 4.837x10^{-8}T^2$$

and $$\log(k(C_2H_2,\ 10)/k\infty) = 0.129 - 1.951x10^{-4}T - 1.97x10^{-7}T^2$$

The uncertainty is a factor of 3.

Table A. Values of $\log(k/k_o)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.05	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03	-0.03	-0.02	-0.02	-0.02
16.5	-0.16	-0.12	-0.11	-0.10	-0.10	-0.09	-0.07	-0.07	-0.06	-0.06	-0.05	-0.05
17.0	-0.23	-0.27	-0.23	-0.21	-0.20	-0.17	-0.15	-0.14	-0.12	-0.11	-0.11	-0.10
17.5	-0.49	-0.49	-0.43	-0.38	-0.36	-0.31	-0.27	-0.25	-0.23	-0.21	-0.20	-0.18
18.0	-0.85	-0.80	-0.70	-0.62	-0.58	-0.51	-0.45	-0.42	-0.38	-0.35	-0.33	-0.30
18.5	-1.28	-1.20	-1.05	-0.91	-0.87	-0.77	-0.69	-0.66	-0.58	-0.54	-0.51	-0.47
19.0	-1.75	-1.66	-1.46	-1.29	-1.22	-1.10	-1.00	-0.94	-0.85	-0.78	-0.74	-0.68
19.5	-2.24	-2.14	-1.92	-1.72	-1.63	-1.49	-1.37	-1.29	-1.18	-1.09	-1.03	-0.96
20.0	-2.74	-2.63	-2.40	-2.19	-2.08	-1.93	-1.69	-1.69	-1.57	-1.46	-1.38	-1.30
20.5	-3.24	-3.13	-2.89	-2.68	-2.56	-2.40	-2.15	-2.15	-2.00	-1.89	-1.79	-1.60
21.0	-3.74	-3.63	-3.39	-3.18	-3.05	-2.89	-2.63	-2.63	-2.47	-2.34	-2.25	-2.05

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.33	0.53	0.71	0.84
500	0.08	0.20	0.38	0.58	0.75
700	0.049	0.13	0.28	0.48	0.67
900	0.032	0.09	0.22	0.40	0.60
1100	0.022	0.067	0.17	0.34	0.54
1300	0.016	0.05	0.14	0.29	0.49
1500	0.012	0.04	0.11	0.25	0.44
1700	0.0095	0.032	0.091	0.21	0.40
1900	0.0075	0.025	0.076	0.19	0.36
2100	0.006	0.021	0.063	0.16	0.33
2300	0.0049	0.017	0.054	0.14	0.30
2500	0.0041	0.014	0.046	0.12	0.27

(W. Tsang, October 1984)

References

Frank, P., and Just, Th., "High Temperature Thermal Decomposition of Acetylene and Diacetylene at Low Relative Concentrations," Combust. Flame 38, 231 (1980)

Tanzawa, T., and Gardiner, W. C., Jr., "Thermal Decomposition of Acetylene," Symp. Combust. 17, (Combustion Institute, Pittsburgh, Pa., 1979) 563

20,2 $C_2H_2 + H_2 \rightarrow C_2H_4$ (a)
$\rightarrow C_2H_3 + H$ (b)

$\log K_p(a) = 7.16094 + 9929.79/T - 136850.9/T^2 + .191006\times10^7/T^3$

$\log K_p(b) = 0.07627 - 14215/T - 52582.9/T^2 + 2.54237\times10^6/T^3$

Comments and Recommendations

There are no direct measurements on these processes. We have calculated the rate constants from the equilibrium constants and the rate constant of reverse processes (-a) (see 18,1) and (-b), assuming a rate constant for the latter of 3×10^{-12}cm^{3}molecule^{-1}s^{-1} as in C_2H_5 + H. Thus, $k_a = 5\times10^{-13}\exp(-19600/T)$cm^{3}molecule^{-1}s^{-1} (see pressure dependence in 18,1) and $k_b = 4\times10^{-12}\exp(-32700/T)$cm^{3}molecule^{-1}s^{-1}. The uncertainties are a factor of 3 and 10 respectively.

(W. Tsang, May 1984)

20,3 $C_2H_2 + O_2 \rightarrow C_2H + HO_2$

Comments and Recommendations

There are no direct measurements for this process. Following (Walker, R. W., Reaction Kinetics, A Specialist Report (The Chemical Society, Burlington House, London, 1975) Vol. 1, pg. 161), we estimate the rate expression for the abstraction process to be $2\times10^{-11}\exp(-37500/T)$cm^{3}molecule^{-1}s^{-1}, with an uncertainty of a factor of 10.

There is also the possibility of a low lying decomposition channel involving O_2 addition and rearrangement prior to decomposition. We are not able to make any prediction regarding the likelihood of such a process.

(W. Tsang, May 1983)

20,4 $C_2H_2 + H + M \rightarrow C_2H_3 + M$ (a)

$\rightarrow C_2H + H_2$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
(a) Payne, Stief (1976)	193-400	$2.4\text{-}168\times10^{17}$	$k_a^{\infty} = 9.2\times10^{-12}\exp(-1213/T)$	1.2
(b) Frank, Just (1980)	1850-3000	$3.6\text{-}16.8\times10^{18}$ Ar	$k_b = 1.3\times10^{-9}\exp(-12900/T)$	5
(a) Sugawara, et al. (1981)	206-461	$5\text{-}6\times10^{19}$ H_2	$k_a^{\infty} = 3.8\times10^{-11}\exp(-1375/T)$	1.3

Comments and Recommendations

(a) The investigations of Sugawara et al. and Payne and Stief cover extended pressure and temperature ranges. Within a factor of 2 to 3, they are in reasonable accord with other workers (summarized in their papers). We have carried out RRKM calculations in order to reproduce their results and this yields: $k_o = 10^{-16.93}(1/T)^{3.75}\exp(-2430/T)cm^6molecule^{-2}s^{-1}$. Pressure dependence and collision efficiencies as a function of step size down can be found in Tables A and B. The data of Payne and Stief are compatible with a step size of down-100 cm^{-1} for He as a third body. We suggest the use of downward step sizes of 300-400 cm^{-1} for Ar and N_2 and 1000-2000 cm^{-1} for larger polyatomics. On this basis we find for step size down of 450 cm^{-1} and with N_2 as the third body:

$k(N_2, 0) = 10^{-6.98}T^{-7.27}\exp(-3632/T)cm^6molecule^{-1}s^{-1}$

$\log(k(N_2, 0.1)/k(N_2, 0)) = -1.689 + 2.889\times10^{-3}T - 1.642\times10^{-6}T^2 + 3.045\times10^{-10}T^3$

$\log(k(N_2, 1)/k(N_2, 0)) = -3.000 + 4.676\times10^{-3}T - 2.511\times10^{-6}T^2 + 4.497\times10^{-10}T^3$

$\log(k(N_2, 10)/k(N_2, 0)) = -4.347 + 5.9911\times10^{-3}T - 2.9544\times10^{-6}T^2 + 4.9944\times10^{-10}T^3$

For C_2H_3 or a similar polyatomic as the bath molecule and with a step size of 1000 cm^{-1}:

$k(C_2H_3, 0) = 10^{-8.11}T^{-6.73}\exp(-3590/RT)cm^6molecule^{-2}s^{-1}$

$\log(k(C_2H_3, 0.1)/k(C_2H_3, 0)) = -1.970 + 3.090\times10^{-3}T - 1.671\times10^{-6}T^2 + 3.012\times10^{-10}T^3$

$\log(k(C_2H_3, 1)/k(C_2H_3, 0)) = -3.277 + 4.636\times10^{-3}T - 2.347\times10^{-6}T^2 + 4.056\times10^{-10}T^3$

$\log(k(C_2H_3, 10)/k(C_2H_3, 0)) = -4.522 + 5.544\times10^{-3}T - 2.505\times10^{-6}T^2 + 3.990\times10^{-10}T^3$

The uncertainty is a factor of 4. Note that at temperatures above 1300 K the reaction is near the low pressure limit.

The rate expression given for (b) by Frank and Just is based on a review of past work. We have used the rate expression for the reverse reaction (21,2) derived on the basis of measured numbers at room temperature and a BSBL calculation and the equilibrium constant to derive $k = 10^{-10}\exp(-11200/T)cm^3molecule^{-1}s^{-1}$.

Table A. Values of $\log(k/k_o)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.14	-0.10	-0.08	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.02	-0.02	-0.02
16.5	-0.28	-0.19	-0.16	-0.12	-0.10	-0.09	-0.08	-0.06	-0.06	-0.04	-0.04	-0.03
17.0	-0.48	-0.34	-0.27	-0.22	-0.18	-0.16	-0.14	-0.11	-0.10	-0.07	-0.07	-0.06
17.5	-0.76	-0.55	-0.44	-0.36	-0.30	-0.25	-0.22	-0.18	-0.16	-0.12	-0.11	-0.09
18.0	-1.15	-0.83	-0.64	-0.54	-0.45	-0.38	-0.32	-0.27	-0.23	-0.18	-0.16	-0.14
18.5	-1.67	-1.17	-0.94	-0.76	-0.64	-0.53	-0.46	-0.38	-0.33	-0.26	-0.23	-0.20
19.0	-2.13	-1.56	-1.26	-1.04	-0.87	-0.73	-0.63	-0.52	-0.46	-0.37	-0.33	-0.28
19.5	-2.61	-1.99	-1.64	-1.37	-1.14	-0.98	-0.85	-0.71	-0.62	-0.52	-0.46	-0.39
20.0	-3.10	-2.46	-2.07	-1.75	-1.47	-1.28	-1.12	-0.95	-0.83	-0.71	-0.63	-0.55
20.5	-3.60	-2.94	-2.53	-2.18	-1.88	-1.64	-1.42	-1.24	-1.10	-0.95	-0.85	-0.75
21.0	-4.10	-3.43	-3.02	-2.64	-2.30	-2.05	-1.80	-1.59	-1.42	-1.25	-1.12	-1.00

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.69	0.83
500	0.069	0.17	0.35	0.55	0.72
700	0.037	0.10	0.24	0.43	0.63
900	0.022	0.066	0.17	0.34	0.54
1100	0.013	0.043	0.12	0.26	0.46
1300	$8.5x10^{-3}$	0.028	0.083	0.20	0.38
1500	$5.6x10^{-3}$	0.019	0.059	0.15	0.32
1700	$3.7x10^{-3}$	0.013	0.042	0.12	0.26
1900	$2.5x10^{-3}$	$9x10^{-3}$	0.03	0.087	0.21
2100	$1.7x10^{-3}$	$6.2x10^{-3}$	0.021	0.065	0.17
2300	$1.2x10^{-3}$	$4.3x10^{-3}$	0.015	0.048	0.12
2500	$7.9x10^{-4}$	$3.0x10^{-3}$	0.011	0.035	0.10

(W. Tsang, October 1984)

References

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Sugawara, K., Okazaki, K., and Sato, S., "Temperature Dependence of the Rate Constants of H and D-atoms Additions to C_2H_4, C_2H_3D, C_2D_4, C_2H_2 and C_2D_2," Bull. Chem. Soc. Jpn. 54, 2872 (1981)

20,5 $C_2H_2 + O \rightarrow CH_2 + CO$ (a)
$\rightarrow C_2HO + H$ (b)

Reference	Conditions Temp./K	Conditions [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Herron, Huie (1973) evaln.	200-700		$k = 2.3\times10^{-11}\exp(-1500/T)$	1.3
Westenberg, deHaas (1977)	297	$(3-14)\times10^{17}$ Ar	$k = 1.2\times10^{-13}$	1.5
Vandooren, Van Tiggelen (1977)	700-1430	4×10^{17}	$k_a = 1.1\times10^{-10}\exp(-2000/T)$	2.5
Vinckier, Debruyn (1979)	290-600	5×10^{16}	$E_{act} = 3.2\pm0.2$ kcal mol^{-1}	
Aleksandrov, et al. (1981)	298-608	2×10^{16}	$k = 3\times10^{-11}\exp(-1625/T)$ $k_b = 1.5\times10^{-11}\exp(-2285/T)$	
Löhr, Roth (1981)	1500-2570	7×10^{17} Ar	$k_a = 2.0\times10^{-10}\exp(-3300/T)$ $k_b = 7.2\times10^{-10}\exp(-6100/T)$	2 2
NASA (1985) evaln.	200-450 298		$k = 2.9\times10^{-11}\exp(-1600/T)$ $k = 1.4\times10^{-13}$	1.5 1.3

Comments and Recommendations

This evaluation accepts the NASA (1985) recommendation. Within the stated error limits it should be valid up to 700 K. The results of Aleksandrov et al. are in extremely good agreement. Up to at least 600 K the predominant reaction channel appears to be that giving CH_2 + CO as products with a minor contribution from the channel giving C_2HO + H (see Blumenberg et al. (1977)) and Aleksandrov et al. (1981), although in a molecular beam study both channels were said to be important (Kanofsky et al. (1974). The high temperature results of Lohr and Roth for k_a agree well with those of Vandooren and Van Tiggelen at 1500 K. More high temperature data are needed.

(R. F. Hampson, July 1985)

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20,6 $C_2H_2 + OH \rightarrow C_2H + H_2O$ (a)
$\rightarrow$ products (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
CODATA (1984) evaln.	200-300		$6.5x10^{-12}exp(-650/T)$ (high pressure limit)	2
	298		$7.3x10^{-13}$	

Comments and Recommendations

The recommended rate expression for the abstraction reaction is $k_a = 2.4x10^{-20}T^{2.68}exp(-6060/T)$ $cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 10. It is derived from a calculation using the BEBO method as described by Brown (1981). This is the predominant reaction under combustion conditions. Near room temperature, where there is little agreement on the mechanism, the rate constant, or its pressure dependence, the recommended expression is that given in the CODATA(1984) evaluation. It is based on results reported in Michael et al. (1980), Perry et al. (1977) and Perry and Williamson (1982).

(R. F. Hampson, May 1983)

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Perry, R. A., and Williamson, D., "Pressure and Temperature Dependence of the OH Radical Reaction with Acetylene," Chem. Phys. Lett. 93, 331 (1982)

20,7 $C_2H_2 + HO_2 \rightarrow CH_2{=}C{=}O + OH$ (a)
$\rightarrow CH_2 + CO + OH$ (b)
$\rightarrow HC_2O + H + OH$ (c)

Comments and Recommendations

There are no measurements for the rate constants of these reactions. We suggest as a very rough approximation, with an uncertainty of at least a factor of 10, the same rate expression as for ethylene reacting with HO_2, $k_a = 1x10^{-14}exp(-4000/T)cm^3molecule^{-1}s^{-1}$. Reaction paths b and c are also possible. We are unable to estimate branching ratios.
(W. Tsang, May 1983)

20,14 $C_2H_2 + CO \rightarrow C_2H + HCO$

Comments and Recommendations

Since there are no measurements for this reaction we have assumed a reverse rate of $3.3x10^{-11}cm^3molecule^{-1}s^{-1}$ to obtain $8x10^{-10}exp(-53700/T)$ for the forward rate constant with an uncertainty of a factor of 10. This makes it an extremely unlikely process under all combustion conditions.
(W. Tsang, May 1983)

20,16 $C_2H_2 + CH_3 \rightarrow C_3H_5$ (a)
$\rightarrow CH_4 + C_2H$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
log $K_p = -0.8887 - 3718.9/T - 316484/T^2 + 4.332x10^7/T^3$ (b)				
Holt, Kerr (1977) (a)	379-487	~$2x10^{18}$ $i\text{-}C_4H_8$, ~0.5-8% C_2H_2, ~1% biacetyl	$1x10^{-12}exp(-3877/T)$	1.4

Comments and Recommendations

The predominant reaction at low temperature is addition. However at higher temperatures the reaction is reversible. Under combustion conditions the abstraction process is the predominant pathway and, within an uncertainty factor of 5, the rate expression is

$$k(CH_3 + C_2H_2 \rightarrow CH_4 + C_2H) \simeq 3x10^{-13}exp(-8700/T)cm^3molecule^{-1}s^{-1}$$

derived on the basis of the reverse rate and equilibrium constant. See data sheet [21,10].
(W. Tsang, May 1983)

References

Holt, P. M., and Kerr, A. J., "Kinetics of Gas Phase Addition Reactions of Methyl Radicals. I. Addition to Ethylene, Acetylene, and Benzene," Int. J. Chem. Kinet. 9, 185 (1977)

20,17 $C_2H_2 + C_2H_5 \rightarrow C_2H + C_2H_6$ (a)
$\rightarrow C_4H_7$ (b)

$\log K_p = -1.20495 - 4740.87/T - 311418.9/T^2 + 4.551646 \times 10^7/T^3$ (a)

Comments and Recommendations

There are no direct measurements on this reaction. We have used the equilibrium constant and results on the reverse reaction [21,11] to derive $k(C_2H_2 + C_2H_5 \rightarrow C_2H + C_2H_6) = 4.5 \times 10^{-13}\exp(-11800/T)$ with an uncertainty of a factor of 5. Note that at lower temperatures the addition reaction (b) is the main process. However, as the temperature is increased the decomposition process will become even more important.

(W. Tsang, May 1984)

20,18 $C_2H_2 + C_2H_4 \rightarrow 2C_2H_3$

$\log K_p = 1.21776 - 14783.99/T - 188722.9/T^2 + 2.216286 \times 10^7/T^3$

Comments and Recommendations

There are no direct measurements for this reaction. We suggest the rate expression $4 \times 10^{-11}\exp(-34400/T)\mathrm{cm^3 molecule^{-1} s^{-1}}$ with an uncertainty of a factor of 10. This is based on the equilibrium constant, a disproportionation to combination ratio of 0.1 and a vinyl combination rate similar to that for ethyl radicals. See (19,19) on vinyl combination and disproportionation.

(W. Tsang, May 1983)

20,20 $C_2H_2 + C_2H_2 \rightarrow C_2H_3 + C_2H$ (a)
$\rightarrow C_4H_3 + H$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
$\log K_p = 0.69769 - 18121/T - 402707.9/T^2 + 5.308452 \times 10^7/T^3$ (a)				
Back (1971)			$k_a = 8.3 \times 10^{-9}\exp(-35250/T)$	
Tanzawa, Gardiner (1979)			$k_b = 1.6 \times 10^{-11}\exp(-23100/T)$	

Comments and Recommendations

There are no direct measurements on these processes. Back's results are based on an assumed disproportionation to combination ratio of 1.0 and a combination rate equal to that of ethyl+ethyl ($1.6 \times 10^{-11}\mathrm{cm^3 molecule^{-1} s^{-1}}$) and the thermodynamics of the process. The results of Tanzawa and Gardiner are from complex shock tube experiments. We have recalculated, following Back's

procedure, but using a disproportionation/combination ratio of 0.1 and newer thermodynamic data and derived $k(C_2H_2 + C_2H_2 \rightarrow C_2H_3 + C_2H) = 1.6\times10^{-11}\exp(-42500/T)\mathrm{cm^3molecule^{-1}s^{-1}}$ with an uncertainty of a factor of 5. Reaction (b) is likely to be a composite process.
(W. Tsang, May 1983)

References

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Tanzawa, T., and Gardiner, W. C., Jr., "Thermal Decomposition of Acetylene," Symp. Combust. 17, (Combustion Institute, Pittsburgh, 1979) 563

21,2 $C_2H + H_2 \rightarrow C_2H_2 + H$

Reference	Conditions Temp./K	 [M]/molecule $\mathrm{cm^{-3}}$	Reaction rate constant, $k/\mathrm{cm^3molecule^{-1}s^{-1}}$	Uncertainty factor
Lange and Wagner (1975)	320	1.3×10^{17} He	1.7×10^{-13}	1.3
Laufer, Bass (1979)	300	1.6×10^{18} He	1.5×10^{-13}	1.3
Okabe (1981)	298		(relative to k(C_2H + C_2H_2)) k/k_{ref}=0.0078 k_{ref}: C_2H + C_2H_2	
Renlund, et al. (1981)	300	2.6×10^{16} He	1.2×10^{-11}	
Brown, Laufer (1981)			$1.9\times10^{-11}\exp(-1450/T)$	calculated

Comments and Recommendations

The expression given by Brown and Laufer (1981) is recommended. They calculated a preexponential factor by the bond energy - bond order (BEBO) method and combined this with the value of k at 300 K reported by Laufer and Bass to give this Arrhenius expression. They also showed that the derived temperature dependence is in good agreement with that calculated by the bond strength - bond length (BSBL) method of Bèrces and Dombi (1980) but is much less than that calculated by the BEBO method. The experimental results of Lange and Wagner (1975) by the discharge flow - mass spectrometric technique are in good agreement with those of Laufer and Bass (1979) who measured the decreased absorption of butadiyne from the reaction $C_2H + C_2H_2 \rightarrow C_4H_2 + H$ upon addition of H_2 in the vacuum ultraviolet flash photolysis of C_2H_2. The recent results of Renlund et al. (1981) by time-resolved CH chemiluminescence are much higher and probably refer to the reaction of excited states of C_2H. Estimated uncertainties are ±30% at room temperatures and increasing to a factor of 3 at 2500 K.
(R. F. Hampson, May 1983)

References

Bèrces. T., and Dombi, J., "Evaluation of the Rate Coefficients and Arrhenius Parameters of Hydrogen Atom Transfer Reactions. I. The Method," Int. J. Chem. 123 (1980); ibid "II. Application of the Method," Int. J. Chem. Kinet. 12, 183 (1980)

Brown, R. L., and Laufer, A. H., "Calculation of Activation Energies for Hydrogen-atom Abstractions by Radicals Containing Carbon Triple Bond," J. Phys. Chem. 85, 3826 (1981)

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Okabe, H., "Photochemistry of Acetylene at 147 nm," J. Chem. Phys. 75, 2772 (1981)

Renlund, A. M., Shokoohi, F., Reisler, H., and Wittig, C., "Gas-Phase Reactions of $C_2H(\tilde{X}\Sigma^+)$ with O_2, H_2, and CH_4 Studies Via Time Resolved Product Emissions," Chem. Phys. Lett. 84, 293 (1981)

21,3 $C_2H + O_2 \rightarrow CO + HCO$ (a)

$\rightarrow HC_2O + O$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Lange, Wagner (1975)	320	1.3×10^{17} He	$k=5.5\times10^{-12}$	1.3 see comments
Renlund, et al. (1981)	300	2.6×10^{16} He	$k=2.1\times10^{-11}$	
Laufer, Lechleider (1984)	300		$k_a=4.0\times10^{-12}$ $k_b=1.0\times10^{-12}$	

Comments and Recommendations

The results of Laufer and Lechleider (1984) using flash photolysis-vacuum ultraviolet spectroscopy techniques are recommended. They are consistent with the results of Lange and Wagner (1975) for the overall rate by the discharge flow-mass spectrometer technique. Renlund et al's recent results by time-resolved chemiluminescence are much higher and probably refer to the reaction of excited states of C_2H. There is considerable uncertainty regarding the nature of the products. These may also include $CH + CO_2$ or $C_2O + OH$. We estimate the experimental uncertainties at ±30%. In the absence of measurements on the temperature dependence we assign a factor of 10 uncertainty at 2500 K. (R. F. Hampson, May 1984)

References

Lange, W., and Wagner, H. Gg., "Massenspektrometrische Untersuchungen über Erzeugung und Reaktionen von C_2H-Radikalen," Ber. Bunsenges. Phys. Chem. 79, 165 (1975)

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Renlund, A. M., Shokoohi, F., Reisler, H., and Wittig, C., "Reaction of C_2H with O_2: Chemiluminescent Products," J. Phys. Chem. 86, 4165 (1982)

21,4 $C_2H + H + M \rightarrow C_2H_2 + M$ (a)

$C_2H + H \rightarrow C_2 + H_2$ (b)

Comments and Recommendations

There are no direct measurements on this process. On the basis of the reverse process and the thermodynamics we have obtained $k_a = 10^{-17.9}(1/T)^{3.1}\exp(-721/T)\mathrm{cm^6 molecule^{-2} s^{-1}}$ [third order] with pressure and collisional efficiencies as given in Tables A and B. We recommend use of a 300 $\mathrm{cm^{-1}}$ downward step size for argon and N_2 and a 1000-2000 $\mathrm{cm^{-1}}$ downward step size for larger polyatomics. On this basis we recommend $k_a\infty = 3\times10^{-10}\mathrm{cm^3 molecule^{-1} s^{-1}}$ with the following pressure corrections:

$$\log(k(N_2,\ 0.1)/k\infty)) = 0.347 - 1.228\times10^{-3}T + 3.435\times10^{-8}T^2$$

$$\log(k(N_2,\ 1)/k\infty)) = 0.005 + 7.854\times10^{-5}T - 1.775\times10^{-7}T^2$$

$$\log(k(N_2,\ 10)/k\infty)) = 0.179 - 3.966\times10^{-4}T - 1.338\times10^{-7}T^2$$

For C_2H_2 and with a step size down of 1000 $\mathrm{cm^{-1}}$, the correction factors are:

$$\log(k(C_2H_2,\ 0.1)/k\infty) = 0.476 - 2.015\times10^{-3}T + 1.908\times10^{-7}T^2$$

$$\log(k(C_2H_2,\ 1)/k\infty) = 0.372 - 1.008\times10^{-3}T - 4.837\times10^{-8}T^2$$

$$\log(k(C_2H_2,\ 10)/k\infty) = 0.129 - 1.951\times10^{-4}T - 1.970\times10^{-7}T^2$$

The uncertainty is a factor of 3.

For reaction (b) a BEBO calculation yields $k_b = 6\times10^{-11}\exp(-14223/T)\mathrm{cm^3 molecule^{-1} s^{-1}}$ with an uncertainty of a factor of 10.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.05	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03	-0.03	-0.02	-0.02	-0.02
16.5	-0.16	-0.12	-0.11	-0.10	-0.10	-0.09	-0.07	-0.07	-0.06	-0.06	-0.05	-0.05
17.0	-0.23	-0.27	-0.23	-0.21	-0.20	-0.17	-0.15	-0.14	-0.12	-0.11	-0.11	-0.10
17.5	-0.49	-0.44	-0.43	-0.38	-0.36	-0.31	-0.27	-0.25	-0.23	-0.21	-0.20	-0.18
18.0	-0.85	-0.80	-0.70	-0.62	-0.58	-0.51	-0.45	-0.42	-0.38	-0.35	-0.33	-0.30
18.5	-1.28	-1.20	-1.05	-0.91	-0.87	-0.77	-0.69	-0.66	-0.58	-0.54	-0.51	-0.47
19.0	-1.75	-1.66	-1.46	-1.29	-1.22	-1.10	-1.00	-0.94	-0.85	-0.78	-0.74	-0.68
19.5	-2.24	-2.14	-1.92	-1.72	-1.63	-1.44	-1.37	-1.29	-1.18	-1.09	-1.03	-0.96
20.0	-2.74	-2.63	-2.40	-2.19	-2.08	-1.93	-1.69	-1.67	-1.57	-1.46	-1.38	-1.30
20.5	-3.24	-3.13	-2.89	-2.68	-2.56	-2.40	-2.15	-2.15	-2.00	-1.89	-1.79	-1.60
21.0	-3.74	-3.63	-3.39	-3.18	-3.05	-2.89	-2.63	-2.63	-2.47	-2.34	-2.25	-2.05

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.33	0.53	0.71	0.84
500	0.08	0.20	0.38	0.58	0.75
700	0.049	0.13	0.28	0.48	0.67
900	0.032	0.09	0.22	0.40	0.60
1100	0.022	0.061	0.17	0.34	0.54
1300	0.016	0.05	0.14	0.29	0.49
1500	0.012	0.04	0.11	0.25	0.44
1700	0.0095	0.032	0.091	0.21	0.40
1900	0.0075	0.025	0.076	0.19	0.36
2100	0.006	0.021	0.063	0.16	0.33
2300	0.0049	0.017	0.054	0.14	0.30
2500	0.0041	0.014	0.046	0.12	0.27

(W. Tsang, October 1984)

21,5 $C_2H + O \rightarrow$ products

Comments and Recommendations

There are no measurements on this process. By analogy with the reactions $O + C_2H_5$ and $O + C_2H_3$ one expects a fast reaction with $k \sim 3\times10^{-11} cm^3 molecule^{-1} s^{-1}$ and highly excited products, possibly CH + CO. The uncertainty is a factor of 3.

(R. F. Hampson, May 1983)

21,6 $C_2H + OH \rightarrow C_2H_2 + O$ (a)
$\rightarrow CH_2 + CO$ (b)

Comments and Recommendations

In the absence of experimental results we suggest that the important reaction will be abstraction or addition followed by decomposition proceeding with a near collisional rate constant of $3\times10^{-11} cm^3 molecule^{-1} s^{-1}$ for each process. The uncertainty is a factor of 10.

(R. F. Hampson, May 1983)

21,7 $C_2H + HO_2 \rightarrow C_2H_2 + O_2$
$\rightarrow HC_2O + OH$

Comments and Recommendations

In the absence of experimental results we suggest that the important reactions will be

abstraction and addition followed by decomposition proceeding with near collisional rate constant of $3\times10^{-11}cm^3molecule^{-1}s^{-1}$ for each process. The uncertainty is a factor of 10.
(R. F. Hampson, May 1983)

21,10 $C_2H + CH_4 \rightarrow C_2H_2 + CH_3$

Reference	Conditions: Temp./K	Conditions: [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981)	297	$(1\text{-}6)\times10^{18}$ He	$(1.2\pm0.2)\times10^{-12}$	1.3
Okabe (1981)	298		$k/k_{ref} = 0.032$ k_{ref}: $C_2H + C_2H_2$	
Renlund, et al. (1981)	300	2.6×10^{16} He	$(4.8\pm1.0)\times10^{-12}$	
Brown, Laufer (1981)			$3\times10^{-12}\exp(-250/T)$	calculated

Comments and Recommendations

The expression given by Brown and Laufer (1981) is recommended. They calculated a preexponential factor by the bond energy-bond order (BEBO) method and combined this with the room temperature value of k reported by Laufer (1981) to give this Arrhenius expression. They also showed that the derived temperature dependence is in good agreement with that calculated by the bond strength-bond length (BSBL) method of Bèrces and Dombi (1980) but is much less than that calculated by the BEBO method. Renlund et al.'s higher results probably refer to the reaction of excited states of C_2H. The estimated uncertainty is a factor of 1.3 at room temperature increasing to a factor of 10 at 2500 K.
(R. F. Hampson, May 1984)

References

Bèrces, T., and Dombi, J., "Evaluation of the Rate Coefficients and Arrhenius Parameters of Hydrogen Atom Transfer Reactions. I. The Method," Int. J. Chem. Kinet. 12, 123 (1980); ibid "II. Application of the Method," Int. J. Chem. Kinet. 12, 183 (1980)

Brown, R. L., and Laufer, A. H., "Calculation of Activation Energies for Hydrogen-atom Abstractions by Radicals Containing Carbon Triple Bond," J. Phys. Chem. 85, 3826 (1981)

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Okabe, H., "Photochemistry of Acetylene at 147 nm," J. Chem. Phys. 75, 2772 (1981)

Renlund, A. M., Shokoohi, F., Reisler, H., and Wittig, C., "Gas-Phase Reactions of $C_2H(X\Sigma^+)$ with O_2, H_2, and CH_4 Studied Via Time-Resolved Product Emissions," Chem. Phys. Lett. 84, 293 (1981)

21,11 $C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981)	297	$(0.6\text{-}23)\times10^{18}$ He	$(6.5\pm0.4)\times10^{12}$	1.3
Brown, Laufer (1981)			6×10^{-12}	calculated

Comments and Recommendations

The expression given by Brown and Laufer (1981) is recommended. They calculated a pre-exponential factor by the bond energy-bond order (BEBO) method and combined this with the room temperature value of k reported by Laufer (1981) to give the temperature-independent expression shown. They also showed that the derived temperature independence is in good agreement with results of calculations by the bond strength-bond length (BSBL) method of Bérces and Dombi (1980) whereas a strong temperature dependence is calculated by the BEBO method. The uncertainties are a factor of 1.3 at room temperature and a factor of 3 at 2500 K.

(R. F. Hampson, May 1984)

References

Bérces, T., and Dombi, J., "Evaluation of the Rate Coefficients and Arrhenius Parameters of Hydrogen Atom Transfer Reactions. I. The Method," Int. J. Chem. Kinet. 12, 123 (1980); ibid "II. Application of the Method," Int. J. Chem. Kinet. 12, 183 (1980)

Brown, R. L., and Laufer, A. H., "Calculation of Activation Energies for Hydrogen-atom Abstractions by Radicals Containing Carbon Triple Bond," J. Phys. Chem. 85, 3826 (1981)

Laufer, A. H., "Reactions of Ethynyl Radicals. Rate Constants with CH_4, C_2H_6, and C_2D_6," J. Phys. Chem. 85, 3828 (1981)

21,14 $C_2H + CO \rightarrow C_2HCO$

Comments and Recommendations

There are no measurements on this system. Since the thermochemistry is also uncertain we suggest using rate constants that we have estimated for the $C_2H_3 + CO + (M) \rightarrow C_2H_3CO$ reaction, $k = 2.5\times10^{-13}\exp(-2420/T)cm^3molecule^{-1}s^{-1}$. Note that at higher temperatures the reaction is reversed. The uncertainty is greater than a factor of 10. Because of this the pressure dependence has been neglected.

(W. Tsang, May 1983)

21,15 $C_2H + HCO \rightarrow C_2H_2 + CO$

Comments and Recommendations

In the absence of experimental results we suggest that the important reaction will be disproportionation proceeding with a near collisional rate constant of 1.0×10^{-10}cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 3.

(R. F. Hampson, May 1983)

21,16 $C_2H + CH_3 \rightarrow C_3H_3 + H$

Comments and Recommendations

Although there are no measurements on this process, the exothermicity of the reaction (~ 117 kJ mol^{-1}) suggests that this will be the preferred channel under practically all combustion situations. We estimate the rate constant for the process to be 4×10^{-11}cm^{3}molecule^{-1}s^{-1}. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

21,17 $C_2H + C_2H_5 \rightarrow C_2H_2 + C_2H_4$ (a)
$\rightarrow C_3H_3 + CH_3$ (b)

Comments and Recommendations

These reactions have not been studied. We estimate $k_a \simeq 3\times10^{-12}$cm^{3}molecule^{-1}s^{-1}, typical of a disproportionation process and $k_b \sim 3\times10^{-11}$cm^{3}molecule^{-1}s^{-1}, a typical rate constant for radical combination. The exothermicity of process (b) ~ 170 kJ mol^{-1} should make this the preferred mode of decomposition (rather than stabilization) for all combustion situations. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

21,18 $C_2H + C_2H_4 \rightarrow C_4H_4 + H$

Comments and Recommendations

In the absence of experimental data, by analogy with the reaction 21,20 $C_2H + C_2H_2$, we suggest this reaction proceeds by a fast addition process with k ~ 2×10^{-11} cm^{3}molecule^{-1}s^{-1} to give an excited C_4H_5 adduct which decomposes to give C_4H_4 (vinyl acetylene) + H. The uncertainty is a factor of 3.

(R. F. Hampson, May 1983)

21,19 $C_2H + C_2H_3 \rightarrow C_4H_4$ (a)

$\rightarrow C_4H_3 + H$ (b)

$\rightarrow C_2H_2 + C_2H_2$ (c)

Comments and Recommendations

There are no experimental data on this system. Assuming the high pressure combination rate to be $3\times10^{-11}cm^3molecule^{-1}s^{-1}$, RRKM calculations indicate that k_{a+b} does not have appreciable pressure dependence. Branching ratios and collision efficiencies are given in Tables A and B. We suggest the use of a step size down of 450 cm^{-1} and 1000 cm^{-1} for weak colliders and large polyatomics respectively. On this basis, we find for N_2:

$\log(k_b/k_a(N_2,\ 0.1)) = 10^{-19.85}T^{6.76}\exp(2021/T)$

$\log(k_b/k_a(N_2,\ 1)) = 10^{-19.02}T^{6.23}\exp(1660/T)$

$\log(k_b/k_a(N_2,\ 10)) = 10^{-22.1}T^{6.95}\exp(1902/T)$

For C_4H_4 using a step size down of 1000 cm^{-1}:

$\log(k_b/k_a(C_4H_4,\ 0.1)) = 10^{-18.1}T^{6.04}\exp(1801/T)$

$\log(k_b/k_a(C_4H_4,\ 1)) = 10^{-21.1}T^{6.72}\exp(2063/T)$

$\log(k_b/k_a(C_4H_4,\ 10)) = 10^{-21.1}T^{6.5}\exp(1747/T)$

Over most of the higher temperature range, decomposition is the predominant mode. We expect an uncertainty of a factor of 2 in the overall rate. Due to the uncertainties in the bond energies we expect an error of a factor of 3 in the branching ratios.

We assign a disproportionation rate(c) of $1.6\times10^{-12}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

Table A. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K					
	300	700	1100	1500	1900	2300
16.0	68	72	140	301	658	958
16.5	22	23	45	98	212	308
17.0	6.9	7.7	15	33	70	101
17.5	2.2	2.7	5.4	11.6	24.5	35
18.0	0.72	0.97	2.1	4.5	9.2	13
18.5	0.24	0.36	0.85	1.9	3.8	5.2
19.0	0.075	0.13	0.34	0.80	1.63	2.2
19.5	0.024	0.04	0.13	0.34	0.72	0.99
20.0	0.01	0.01	0.05	0.14	0.30	0.43
20.5			0.02	0.05	0.12	0.18
21.0			0.01	0.02	0.04	0.07

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.32	0.52	0.70	0.83
700	0.04	0.11	0.26	0.45	0.65
1100	0.016	0.052	0.14	0.29	0.49
1500	7.8×10^{-3}	0.026	0.076	0.19	0.37
1900	3.9×10^{-3}	0.014	0.044	0.12	0.27
2300	2.1×10^{-3}	7.5×10^{-3}	0.026	0.076	0.19

(W. Tsang, October 1984)

21,20 $C_2H + C_2H_2 \rightarrow C_4H_2 + H$

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Lange, Wagner (1975)	320	1.3×10^{17} He	5.0×10^{-11}	1.3
Laufer, Bass (1979)	298	$(0.6-23)\times10^{18}$ He	$(3.1\pm0.2)\times10^{-11}$	1.3
Frank, Just (1980)	2300-2700	6×10^{18}	6×10^{-11}	2

Comments and Recommendations

The recommended value is the mean of the two reported direct experimental values of Lange and Wagner (1975) and Laufer and Bass (1979), i.e. 4×10^{-11}cm^{3}molecule^{-1}s^{-1}. These two results by completely independent techniques are in good agreement. Lange and Wagner used the discharge flow-mass spectrometric technique. Laufer and Bass monitored the build-up of butadiyne in flash photolysis-kinetic spectroscopy experiments. Frank and Just (1980) derived their value by computer modeling of the temporal behavior of H atoms observed by atomic resonance absorption spectrophotometry following the shock tube decomposition of acetylene. All results are in good agreement and suggest a fast addition process and decomposition of excited C_4H_3.

(R. F. Hampson, May 1984)

References

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Laufer, A. H., and Bass, A. M., "Photochemistry of Acetylene. Bimolecular Rate Constant for the Formation of Butadiyne and Reactions of Ethynyl Radicals," J. Phys. Chem. 83, 310 (1979)

21,21 $C_2H + C_2H \rightarrow C_4H_2$ (a)

$\rightarrow C_4H + H$ (b)

$\rightarrow C_2H_2 + C_2$ (c)

Comments and Recommendations

There are no experimental results. Step (b) results from the decomposition of vibrationally excited C_4H_2. Assuming that the general pattern of behavior for C_2H is similar to that for other organic radicals and on the basis of RRKM calculations we find $k_{a+b} \sim 3 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ with branching ratios on the basis of strong collisions as given in Table A. Collision efficiency as a function of step size down and temperature can be found in Table B. It can be seen that under practically all conditions decomposition is favored. We suggest the use of a 450 cm^{-1} step size for argon, N_2 etc. and a 1000 cm^{-1} step size for larger polyatomics. This leads to the following branching ratios at 0.1, 1 and 10 atm of N_2 and diacetylene respectively:

$$\log(k_b/k_a(N_2, 0.1)) = 10^{-16.16} T^{5.55} \exp(1828/T)$$
$$\log(k_b/k_a(N_2, 1)) = 10^{-16.08} T^{5.25} \exp(1611/T)$$
$$\log(k_b/k_a(N_2, 10)) = 10^{-16.08} T^{5.0} \exp(1330/T)$$

$$\log(k_b/k_a(C_4H_2, 0.1)) = 10^{-14.96} T^{5.02} \exp(1699/T)$$
$$\log(k_b/k_a(C_4H_2, 1)) = 10^{-14.74} T^{4.69} \exp(1418/T)$$
$$\log(k_b/k_a(C_4H_2, 10)) = 10^{-15.92} T^{4.81} \exp(1325.5/T)$$

The uncertainty in k_{a+b} is a factor of 2. However, due to the possible error in the bond strength, the branching ratio is uncertain by a factor of 3. The disproportionation reaction is thermoneutral and we suggest the use of $k_c = 3 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 3.

Table A. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K					
	500	900	1300	1700	2100	2500
16.0	127	131	178	214	317	563
17.0	13	13.5	18.8	23	34	60
18.0	1.4	1.7	2.4	3	4.5	7.8
19.0	0.16	0.23	0.38	0.49	0.77	1.3
20.0	0.0017	0.0027	0.0055	0.0081	0.015	0.032
21.0	0.0017	0.0027	0.0055	0.0081	0.015	0.032

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.70	0.83
500	0.076	0.17	0.36	0.57	0.74
700	0.046	0.12	0.27	0.46	0.66
900	0.029	0.084	0.20	0.38	0.59
1100	0.019	0.06	0.15	0.32	0.52
1300	0.013	0.044	0.12	0.27	0.46
1500	0.01	0.033	0.096	0.22	0.41
1700	7.1×10^{-3}	0.026	0.077	0.19	0.37
1900	5.8×10^{-3}	0.02	0.062	0.16	0.32
2100	4.5×10^{-3}	0.016	0.050	0.13	0.29
2300	3.6×10^{-3}	0.012	0.041	0.11	0.25
2500	2.9×10^{-3}	0.010	0.034	0.097	0.23

(W. Tsang, October 1984)

22,1 $CH_3CO + M \rightarrow CH_3 + CO + M$

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}		
Anastasi, Maw (1982)	323	2.2×10^{19} CO	$k = 24.5s^{-1}$	1.3
	343	$(0.3\text{-}2.1)\times10^{19}$ CO	$k\infty = 186s^{-1}$	
			$k_o = 3.1\times10^{-17}$	
Watkins, Word (1974)	260-413	$(1.8\text{-}8)\times10^{19}$ SF_6, CO, azomethane	$k\infty = 1.6\times10^{13}\exp(-8660/T)s^{-1}$	1.3
Frey, Vinall (1973)	325.7	10×10^{17} methyl t-butyl ketone, added N_2	$k = k_{comb}{}^{1/2}/D\ s^{-1}$ where $D = 3.97\times10^{11}/[M] + 3.2\times10^{-7}$ $k_{comb} = k(2CH_3CO \rightarrow (CH_3CO)_2)$	2
Szirovicza, Walsh (1974)	507	$(7\text{-}130)\times10^{17}$ CH_2CO, HI	$k = k_{HI}/D\ s^{-1}$ where $D = 7.41\times10^5/[M] + 7.26\times10^{-17}$ $k_{HI} = k(CH_3CO + HI \rightarrow CH_3CHO + I)$	5
Kerr, Calvert (1965)	338	$(1.2\text{-}2.9)\times10^{18}$ CO, azomethane, neopentane	$k = k_{Me}{}^{1/2}/D\ s^{-1}$ where $D = 3.9\times10^{11}/[M] + 0.64\times10^{-7}$	2
O'Neal, Benson (1962)	508-568	$(3\text{-}21)\times10^{17}$ acetone, HI	$k = 1/(1/k_o[M] + 1/k(\infty))\ s^{-1}$ $k_o = 5\times10^{-10}\exp(-6042/T)$ $k\infty = 2\times10^{10}\exp(-7552/T)s^{-1}$	5

Comments and Recommendations

All experiments are in the fall-off region and except for the results of Anastasi and Maw and Watkins and Word are close to the bimolecular limit. Due to the instability of CH_3CO all the early experimental results are ratios of rates. Even after taking into account possible uncertainties it is not possible to resolve all the data. The experiments divide into two sets, the lower temperature numbers in the 300-400 K range and the higher temperature numbers in the 500-570 K range. We suggest a second order rate expression of the form: $k_o = 10^{3.95}T^{-3.37}\exp(-9503/T)\mathrm{cm^3molecule^{-1}s^{-1}}$. Corrections for second order behavior and collisional efficiencies can be found in Tables A and B.

The results of Anastasi and Maw are commensurate with a downward step size of 300 $\mathrm{cm^{-1}}$ for CO as the third body. We suggest the use of a similar value for N_2 and Argon near room temperature. For temperatures >500 K a value of 450 $\mathrm{cm^{-1}}$ may be more appropriate. For large polyatomics a step size downward of the order of 1000-2000 $\mathrm{cm^{-1}}$ should be used. We estimate an uncertainty of a factor of 3.

Our results reproduce the lower temperature data on the basis of $k(2CH_3CO \rightarrow (CH_3CO)_2) \sim 2\times10^{-11}\mathrm{cm^3molecule^{-1}s^{-1}}$ and are a factor of ~10 and ~25 larger than the measurements of O'Neal and Benson and those of Szirovicza and Walsh respectively with $k(CH_3CO + HI \rightarrow CH_3CHO + I)$ as a basis. Using the high temperature data as a basis and adjusting the reaction threshold would yield large errors for the lower temperature studies unless acetyl radical combination should be a factor of 1000 slower.

The recommended expression for N_2 (450 $\mathrm{cm^{-1}}$ step size down) at the low pressure limit is:

$$k(N_2,\ 0) = 10^{19.16}T^{-8.62}\exp(-11284/T)$$

The correction factors for 1 and 10 atm are:

$$\log(k(N_2,\ 1)/k(N_2,0)) = -0.536 + 8.681\times10^{-4}T - 3.351\times10^{-7}T^2$$

$$\log(k(N_2,\ 10)/k(N_2,\ 0)) = -1.55 + 2.351\times10^{-3}T - 8.685\times10^{-7}T^2$$

For larger polyatomics as a third body, with an assumed step size down of 1500 $\mathrm{cm^{-1}}$ the low pressure limiting rate expression is:

$$k(CH_3CO,\ 0) = 10^{15.95}T^{-7.38}\exp(-11061/T)$$

The correction factors for 1 and 10 atm are:

$$\log(k(CH_3CO,\ 1)/k(\mathrm{poly},\ 0)) = -0.672 + 1.003\times10^{-3}T - 3.662\times10^{-7}T^2$$

$$\log(kCH_3CO,\ 10)/k(\mathrm{poly},\ 0)) = -17.727 + 2.335\times10^{-3}T - 7.954\times10^{-7}T^2$$

We estimate the uncertainty at a factor of 2.

Table A. Values of $\log(k/k_o)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
17.0	-0.01	-0.01	-0.01									
17.5	-0.03	-0.02	-0.02	-0.01	-0.01	-0.01						
18.0	-0.08	-0.06	-0.05	-0.04	-0.03	-0.02	-0.02	-0.01	-0.01	-0.01	-0.01	
18.5	-0.18	-0.14	-0.12	-0.09	-0.07	-0.06	-0.04	-0.03	-0.02	-0.02	-0.01	-0.01
19.0	-0.37	-0.29	-0.24	-0.19	-0.15	-0.12	-0.09	-0.07	-0.05	-0.04	-0.03	-0.02
19.5	-0.65	-0.53	-0.42	-0.34	-0.27	-0.21	-0.17	-0.13	-0.10	-0.08	-0.06	-0.05
20.0	-1.03	-0.84	-0.69	-0.56	-0.46	-0.37	-0.29	-0.23	-0.18	-0.15	-0.12	-0.10
20.5	-1.47	-1.25	-1.04	-0.86	-0.72	-0.59	-0.47	-0.40	-0.33	-0.27	-0.22	-0.18
21.0	-1.94	-1.70	-1.46	-1.25	-1.06	-0.90	-0.75	-0.64	-0.54	-0.47	-0.40	-0.34

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.13	0.28	0.48	0.67	0.81
500	5.2×10^{-2}	0.14	0.29	0.49	0.68
700	2.3×10^{-2}	0.07	0.17	0.35	0.55
900	1.1×10^{-2}	3.5×10^{-2}	0.10	0.23	0.42
1100	5.1×10^{-3}	1.8×10^{-2}	0.06	0.15	0.30
1300	2.4×10^{-3}	8.8×10^{-3}	3×10^{-2}	8.6×10^{-2}	0.20
1500	1.1×10^{-3}	4.3×10^{-3}	1.5×10^{-2}	4.8×10^{-2}	0.13
1700	5.4×10^{-4}	2.0×10^{-3}	7.5×10^{-3}	2.5×10^{-2}	7.6×10^{-2}
1900	2.5×10^{-4}	9.6×10^{-4}	3.6×10^{-3}	1.3×10^{-2}	4.1×10^{-2}
2100	1.1×10^{-4}	4.4×10^{-4}	1.7×10^{-3}	6.3×10^{-3}	2.2×10^{-2}
2300	5.2×10^{-5}	2.0×10^{-4}	7.9×10^{-4}	3.0×10^{-3}	1.1×10^{-2}
2500	2.4×10^{-5}	9.4×10^{-5}	3.7×10^{-4}	1.4×10^{-3}	5.2×10^{-3}

(W. Tsang, October 1984)

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Watkins, K. W., and Word, W. W., "Addition of Methyl Radicals to Carbon Monoxide Chemically and Thermally Activated Decomposition of Acetyl Radicals," Int. J. Chem. Kinet. 6, 855 (1974)

22,2 $CH_3CO + H_2 \rightarrow CH_3CHO + H$

$\log K_p = -1.25914 - 3212.09/T - 7137/T^2 + 0.25841\text{x}10^7/T^3$

Comments and Recommendations

Since there are no data on these reactions we have taken note of the fact that the reaction rates of H + HCHO and rates of $H + CH_3CHO$ at room temperature differ by roughly a factor of 2 arising from the number of H-atoms available for abstraction. Using $(1/2)k(HCHO + H) = 1.82\text{x}10^{-16}T^{1.77}\exp(-1510/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ [12,4] and the equilibrium constant, we derive $k(CH_3CO + H_2 \rightarrow CH_3CHO + H) = 6.8\text{x}10^{-18}T^{1.82}\exp(-8862/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

22,3 $CH_3CO + O_2 \rightarrow CH_3CO_3$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	factor
			$k/k(CH_3CO \rightarrow CH_3 + CO)$:	
Hoare, Whytock (1967)	373	$2.6\text{x}10^{18}$	$1.5\text{x}10^{-15}$ $\text{cm}^3\text{molecule}^{-1}$	5
	423	$(2.3\text{-}23)\text{x}10^{17}$	$1.2\text{x}10^{-16}$ $\text{cm}^3\text{molecule}^{-1}$	
			$k = 3\text{x}10^{-13}$	
McDade, et al. (1982)	298	$(3\text{-}13)\text{x}10^{16}$ He	$k = 3\text{x}10^{-12}$	3

Comments and Recommendations

The recent results of McDade et al. in which the acetyl radical decay was monitored by photoionization mass spectrometry are the only direct measurements of this rate constant. The rate constant did not depend on total pressure over the limited range 1 to 4 torr. Acetyl peroxy radicals were observed in absorption by Hunziker and Wendt when acetyl radicals were generated in the presence of O_2 at 1 atmosphere N_2. The earlier results of Hoare and Whytock were based on competition between this reaction and decomposition of the acetyl radical which is in the pressure dependent falloff region. It is surprising, therefore, that no pressure effect on $k/k(CH_3CO \rightarrow CH_3 + CO)$ was observed unless the reaction with O_2 is also pressure dependent. The newer, direct results of McDade et al. are preferred, but with an uncertainty of a factor of two. Under combustion conditions the reverse reaction will predominate.

(R. F. Hampson, May 1983)

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22,4 $CH_3CO + H \rightarrow CH_2CO + H_2$ (a)
$\rightarrow CH_3 + CHO$ (b)

Comments and Recommendations

In the absence of experimental data, we assume the process will be analogous to that for the reaction $C_2H_5 + H$ where recombination followed by decomposition of the hot adduct with a close to collisional rate constant is dominant, therefore $k_b=1.6x10^{-10}cm^3molecule^{-1}s^{-1}$. On a similar basis we expect $k_a \sim 3x10^{-12}cm^3molecule^{-1}s^{-1}$. The estimated uncertainies are factors of 3.

(W. Tsang, May 1983)

22,5 $CH_3CO + O \rightarrow CH_3 + CO_2$

Comments and Recommendations

There are no direct measurements on this process. By analogy with other O atom reactions with alkyl radicals, it should be fast, $k \sim 1.6x10^{-11}cm^3molecule^{-1}s^{-1}$ and should proceed by an addition mechanism followed by decomposition of the hot adduct. The estimated uncertainty is a factor of 3.

(W. Tsang, May 1983)

22,6 $CH_3CO + OH \rightarrow CH_2CO + H_2O$ (a)
$\rightarrow CH_3COOH^{\dagger} \rightarrow CH_3 + CO + OH$ (b)

Comments and Recommendations

In the absence of direct measurements we estimate that the main reaction will be addition (b) followed by decomposition with an estimated rate constant of $k_b = 5x10^{-11}cm^3molecule^{-1}s^{-1}$. The abstraction reaction (a) will be somewhat slower $k_a = 2x10^{-11}$. The uncertainties are factors of 3.

(W. Tsang, May 1983)

22,7 $CH_3CO + HO_2 \rightarrow CH_3 + CO_2 + OH$

Comments and Recommendations

In the absence of information on this process, we postulate that abstraction will be slow in comparison to combination. The latter will result in the formation of a hot adduct which will rapidly decompose. The rate constant will be close to collisional $\sim 5x10^{-11}cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

22,8 $CH_3CO + H_2O_2 \rightarrow CH_3CHO + HO_2$

$\log K_p = -1.05204 + 859.41/T - 110330.6/T^2 + 1.20225\times10^7/T^3$

Comments and Recommendations

There are no experimental results on this reaction. The rates of HO_2 attack on aldehydic hydrogen are, however, remarkably similar (A. C. Lloyd, Int. J. Chem. Kinet. 6, 169 (1974)). We have accordingly used the rate expression for HO_2 + HCHO and derived the rate for the reverse process. This leads to $k = 3\times10^{-13}\exp(-4140/T)\mathrm{cm^3 molecule^{-1} s^{-1}}$ with an uncertainty factor of 5.

(W. Tsang, May 1983)

22,10 $CH_3CO + CH_4 \rightarrow CH_3CHO + CH_3$

$\log K_p = 0.25098 - 3399.19/T - 40778/T^2 + 0.96779\times10^7/T^3$

Comments and Recommendations

There are no direct measurements. However, from the reverse reaction [reviewed in Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals," (Butterworth, London, 1976)] pg. 151, and the equilibrium constant one obtains $k = 3.6\times10^{-21}T^{2.88}\exp(-10800/T)\mathrm{cm^3 molecule^{-1} s^{-1}}$. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

22,11 $CH_3CO + C_2H_6 \rightarrow C_2H_5 + CH_3CHO$

$\log K_p = 0.56723 - 2377.22/T - 45843/T^2 + 0.74821\times10^7/T^3$

Comments and Recommendations

In the absence of direct measurements we have used the rate expression for $C_2H_5 + H_2CO$, divided by 2 to take into account the reaction degeneracy, and from the equilibrium constant obtained $k = 3\times10^{-20}T^{2.75}\exp(-8820/T)\mathrm{cm^3 molecule^{-1} s^{-1}}$. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

22,12 $CH_3CO + HCHO \rightarrow CH_3CHO + CHO$

Comments and Recommendations

There are no direct experimental results. On the basis of analogous systems we estimate $k = 3\times10^{-13}\exp(-6500/T)\mathrm{cm^3 molecule^{-1} s^{-1}}$ with an uncertainty of a factor of 10.

(W. Tsang, May 1983)

22,15 $CH_3CO + HCO \rightarrow CH_3CHO + CO$ (a)
$\rightarrow CH_3COCHO$ (b)

Comments and Recommendations

There are no direct measurements on this process. We assume that process (a) (disproportionation) will be similar to the $HCO + HCO \rightarrow H_2CO + CO$ reaction and thus assign a rate constant of 1/2 this value, $k_a = 1.5\times10^{-11}cm^3molecule^{-1}s^{-1}$. The combination process is assigned a rate constant of $k_b = 3\times10^{-11}cm^3molecule^{-1}s^{-1}$. Uncertainties are factors of 3.

(W. Tsang, May 1983)

22,16 $CH_3CO + CH_3 \rightarrow CH_3COCH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Anastasi, Maw (1982)	263-343	$(0.3\text{-}2.1)\times10^{19}$ CO	4×10^{-11}	1.5
Parkes (1981)	298	2.1×10^{19} CO	7×10^{-11}	1.5
Adachi, et al. (1981)	298	4.8×10^{18} acetone	1.4×10^{-10}	2
Adachi, et al. (1978)	298	4.8×10^{18} acetone	1.3×10^{-10}	2

Comments and Recommendations

We have used the data of Parkes and an estimated A-factor of the reverse reaction of 5×10^{16} s^{-1} at 1100 K and the equilibrium constant to derive $k = 7\times10^{-11}(300/T)^{-0.8}cm^3molecule^{-1}s^{-1}$ The pressure and temperature dependences for strong colliders are given in Table A. Collision efficiency as a function of temperature and step size can be found in Table B. Unfortunately, there are no direct measurements at combustion temperatures. We suggest the use of 200-400 cm^{-1} downward step sizes for Ar and N_2 and 1000-2000 cm^{-1} for strong colliders. Adachi et al. also report the displacement process $CH_3 + COCH_3 \rightarrow C_2H_6 + CO$ with a rate constant 38% of that for combination. Further verification is needed. For N_2 and acetone at 0.1, 1, and 10 atm, the following correction should be used:

$$\log(k(N_2,0.1)/k\infty) = 0.458 + 2.135\times10^{-3}T - 2.497\times10^{-6}T^2 + 3.963\times10^{-10}T^3$$

$$\log(k(N_2,\ 1)/k\infty) = -0.444 + 1.802\times10^{-3}T - 1.712\times10^{-6}T^2 + 1.925\times10^{-10}T^3$$

$$\log(k(N_2,\ 10)/k\infty) = -0.272 + 9.596\times10^{-4}T - 6.801\times10^{-7}T^2 - 3.984\times10^{-11}T^3$$

where we have used a step size down of 350 cm^{-1} and:

$$\log(k(CH_3COCH_3,0.1)/k\infty) = -0.406 + 1.731\times10^{-3}T - 1.765\times10^{-6}T^2 + 2.197\times10^{-10}T^3$$

$$\log(k(CH_3COCH_3,\ 1)/k\infty) = -0.287 + 1.060\times10^{-3}T - 8.363\times10^{-7}T^2 + 4.144\times10^{-12}T^3$$

$$\log(k(CH_3COCH_3,\ 10)/k\infty) = -0.089 + 2.211\times10^{-4}T + 4.2523\times10^{-8}T^2 - 1.721\times10^{-10}T^3$$

where we have used a step size down of 1000 cm^{-1}. The uncertainty is a factor of 3.

Table A. Values of $\log(k/k_0)$: dependence on concentration and temperature.

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.05	-0.21	-0.46	-0.76	-1.09	-1.44	-1.79	-2.14	-2.48	-2.81	-3.10
16.5	-0.02	-0.12	-0.29	-0.53	-0.81	-1.11	-1.44	-1.76	-2.07	-2.38	-2.67
17.0	-0.01	-0.06	-0.17	-0.35	-0.57	-0.84	-1.12	-1.41	-1.70	-1.98	-2.24
17.5		-0.03	-0.09	-0.21	-0.38	-0.60	-0.83	-1.09	-1.34	-1.60	-1.84
18.0		-0.01	-0.04	-0.11	-0.23	-0.40	-0.59	-0.80	-1.02	-1.24	-1.46
18.5			-0.02	-0.06	-0.13	-0.25	-0.39	-0.56	-0.74	-0.93	-1.11
19.0			-0.01	-0.02	-0.06	-0.14	-0.24	-0.36	-0.50	-0.65	-0.80
19.5				-0.01	-0.027	-0.07	-0.13	-0.21	-0.31	-0.42	-0.53
20.0					-0.01	-0.03	-0.06	-0.11	-0.17	-0.24	-0.32
20.5						-0.01	-0.03	-0.05	-0.08	-0.12	-0.17
21.0							-0.01	-0.02	-0.03	-0.05	-0.08

Table B. Collision efficiency β_c as a function of downward step size.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
700	3.3×10^{-2}	9.5×10^{-2}	0.22	0.41	0.61
900	1.8×10^{-2}	5.7×10^{-2}	0.15	0.31	0.51
1100	1.1×10^{-2}	3.4×10^{-2}	9.9×10^{-2}	0.23	0.42
1300	6.7×10^{-3}	2.2×10^{-2}	6.5×10^{-2}	0.17	0.34
1500	3.7×10^{-3}	1.3×10^{-2}	4.3×10^{-2}	0.12	0.26
1700	2.2×10^{-3}	8×10^{-3}	2.7×10^{-2}	7.9×10^{-2}	0.19
1900	1.2×10^{-3}	4.8×10^{-3}	1.7×10^{-2}	5.3×10^{-2}	0.14
2100	7.3×10^{-4}	2.8×10^{-3}	1×10^{-2}	3.3×10^{-2}	9.5×10^{-2}
2300	4.1×10^{-4}	1.6×10^{-3}	5.8×10^{-3}	2×10^{-2}	6.2×10^{-2}
2500	2.2×10^{-4}	8.5×10^{-4}	3.2×10^{-3}	1.2×10^{-2}	3.8×10^{-2}

(W. Tsang, October 1984)

References

Adachi, H., Basco, N., and James, D. G. L., "The Acetyl Radicals CH_3CO and CD_3CO Studied by Flash Photolysis and Kinetic Spectroscopy," Int. J. Chem. Kinet. 13, 1251 (1981)

Adachi, H., Basco, N., and James, D. G. L., "The Acetyl Radical Studied by Flash Photolysis and Kinetic Spectroscopy," Chem. Phys. Lett. 59, 502 (1978)

Anastasi, C., and Maw, P. R., "Reaction Kinetics in Acetyl Chemistry over a Wide Range of Temperature and Pressure," J. Chem. Soc. Faraday Trans. I 78, 2423 (1982)

Parkes, D. A., "The Ultraviolet Absorption Spectra of the Acetyl Radical and the Kinetics of the CH_3 + CO Reaction at Room Temperature," Chem. Phys. Lett. 77, 527 (1981)

22,17 $CH_3CO + C_2H_5 \rightarrow C_2H_5COCH_3$

Comments and Recommendations

In the absence of experimental results we suggest a rate constant expression similar to that for $CH_3CO + CH_3 \rightarrow CH_3COCH_3$, $k = 3\text{x}10^{-11}(300/T)^{1/2}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, May 1983)

22,19 $CH_3CO + C_2H_3 \rightarrow CH_3 + C_2H_3CO$

Comments and Recommendations

In the absence of experimental data we assume that the primary reaction mechanism will be that of addition followed by decomposition of the hot adduct. The rate constant will be close to collisional ~ $3\text{x}10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, May 1983)

22,21 $CH_3CO + C_2H \rightarrow C_2HCO + CH_3$

Comments and Recommendations

In the absence of experimental results we suggest that the important reaction will be addition followed by decomposition of the hot adduct. The rate constant will be close to collisional ~ $3\text{x}10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, May 1983)

22,22 $CH_3CO + CH_3CO \rightarrow CH_3COCOCH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Anastasi, Maw (1982)	263-343	$(0.3\text{-}3)\text{x}10^{19}$	$0.9\text{-}1.3\text{x}10^{-11}$	1.5
Parkes (1981)	298	$(0.3\text{-}2.5)\text{x}10^{19}$	$3\text{x}10^{-11}$	1.5
Adachi, et al. (1978)	298	$0.2\text{x}10^{18}$	$7.5\text{x}10^{-11}$	2
Szirovicza, Walsh (1974)	507	$(7\text{-}130)\text{x}10^{17}$ CH_2CO, HI	$4\text{x}10^{-13}$	2
Benson, O'Neal (1970)	508-568	$(3\text{-}21)\text{x}10^{17}$ acetone, HI	$5\text{x}10^{-13}$	large

Comments and Recommendations

All of the direct measurements favor the high rates that are characteristic of radical combination. We suggest $k = 2\text{x}10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty factor of 2.

(W. Tsang, May 1983)

References

Adachi, H., Basco, N., and James, D. G. L., "The Acetyl Radical Studied by Flash Photolysis and Kinetic Spectroscopy," Chem. Phys. Lett. 59, 502 (1978)

Anastasi, C., and Maw, P. R., "Reaction Kinetics in Acetyl Chemistry over a Wide Range of Temperature and Pressure," J. Chem. Soc., Faraday Trans. I 78, 2423 (1982)

Benson, S. W., and O'Neal, H. E., "Kinetic Data on Gas Phase Unimolecular Reactions," NBS-NSRDS-21 (1970) 424 (Supt. Doc., U.S. Govt. Printing Office, Washington D.C. 20402)

Parkes, D. A., "The Ultraviolet Absorption Spectra of the Acetyl Radical and the Kinetics of the CH_3 + CO Reaction at Room Temperature," Chem. Phys. Lett. 77, 527 (1981)

Szirovicza, L., and Walsh, R., "Gas Phase Addition of HI to Ketene and the Kinetics of Decomposition of the Acetyl Radical," J. Chem. Soc., Faraday Trans. I 70, 33 (1974)

23,1 CH_3O_2 (+M) → CH_3 + O_2 (+M)

Comments and Recommendations

There have not been any direct measurements on this process.

We have used low temperature measurement for the reverse process (see 16,3) and thermodynamics to derive the bimolecular rate expression $k(CH_3O_2 + M \rightarrow CH_3 + O_2 + M) = 10^{12.00}T^{-5.44}\exp(-15257/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$ assuming strong collisions. The enthalpies are, however, uncertain to 20 kJ mol^{-1} and we have assumed that the reverse process has no activation energy. Actually, the entire process is in the intermediate pressure region. Table A defines the departure from the bimolecular region. Collision efficiency as a function of step size and temperature can be found in Table B. Assuming that step size down for N_2 is 450 cm^{-1} and for a polyatomic such as CH_3O_2 is 1000 cm^{-1} we find the limiting low pressure rate expressions to be:

$$k(N_2,\ 0) = 10^{25.1}T^{-10.02}\exp(-16731/T)$$
$$k(CH_3O_2,\ 0) = 10^{23.65}T^{-9.36}\exp(-16604/T)$$

Rate expressions for the pressure dependence are as follows:

$$\log(k/k_o(N_2,\ 0.1)) = -1.313 + 2.496\mathrm{x}10^{-3}T - 1.508\mathrm{x}10^{-6}T^2 + 2.901\mathrm{x}10^{-10}T^3$$
$$\log(k/k_o(N_2,\ 1)) = -2.542 + 4.597\mathrm{x}10^{-3}T - 2.689\mathrm{x}10^{-6}T^2 + 5.062\mathrm{x}10^{-10}T^3$$
$$\log(k/k_o(N_2,\ 10)) = -3.997 + 6.569\mathrm{x}10^{-3}T - 3.603\mathrm{x}10^{-6}T^2 + 6.495\mathrm{x}10^{-10}T^3$$

and for colliders similar to CH_3O_2:

$$\log(k/k_o(CH_3O_2,0.1)) = -1.692 + 3.088\mathrm{x}10^{-3}T - 1.816\mathrm{x}10^{-6}T^2 + 3.434\mathrm{x}10^{-10}T^3$$
$$\log(k/k_o(CH_3O_2,\ 1)) = -3.000 + 5.0826\mathrm{x}10^{-3}T - 2.853\mathrm{x}10^{-6}T^2 + 5.233\mathrm{x}10^{-10}T^3$$
$$\log(k/k_o(CH_3O_2,\ 10)) = -4.3722 + 6.427\mathrm{x}10^{-3}T - 3.237\mathrm{x}10^{-6}T^2 + 5.480\mathrm{x}10^{-10}T^3$$

The uncertainty is a factor of 6.

Table A. Values of $\log(k/k_o)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.13	-0.08	-0.05	-0.03	-0.02	-0.02	-0.01	-0.01	-0.01			
16.5	-0.21	-0.13	-0.09	-0.06	-0.04	-0.03	-0.02	-0.02	-0.01	-0.01	-0.01	
17.0	-0.33	-0.21	-0.14	-0.10	-0.07	-0.05	-0.04	-0.03	-0.02	-0.02	-0.01	-0.01
17.5	-0.50	-0.32	-0.22	-0.16	-0.12	-0.09	-0.07	-0.05	-0.04	-0.03	-0.02	-0.02
18.0	-0.74	-0.49	-0.35	-0.26	-0.19	-0.15	-0.11	-0.09	-0.07	-0.05	-0.04	-0.03
18.5	-1.05	-0.72	-0.53	-0.40	-0.31	-0.24	-0.18	-0.14	-0.11	-0.08	-0.07	-0.05
19.0	-1.44	-1.05	-0.78	-0.60	-0.48	-0.37	-0.30	-0.24	-0.19	-0.14	-0.12	-0.09
19.5	-1.88	-1.42	-1.11	-0.88	-0.71	-0.57	-0.46	-0.37	-0.31	-0.24	-0.20	-0.16
20.0	-2.36	-1.86	-1.51	-1.24	-1.02	-0.85	-0.70	-0.58	-0.48	-0.40	-0.33	-0.29
20.5	-2.85	-2.33	-1.96	-1.66	-1.41	-1.20	-1.02	-0.87	-0.74	-0.64	-0.55	-0.47
21.0	-3.35	-2.83	-2.44	-2.12	-1.85	-1.62	-1.42	-1.25	-1.10	-0.97	-0.86	-0.77

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.29	0.49	0.68	0.82
500	0.056	0.15	0.31	0.51	0.69
700	0.028	0.081	0.20	0.38	0.58
900	0.014	0.045	0.12	0.27	0.47
1100	$7.8\text{x}10^{-3}$	0.026	0.078	0.19	0.36
1300	$4.3\text{x}10^{-3}$	0.015	0.047	0.13	0.28
1500	$2.3\text{x}10^{-3}$	$8.5\text{x}10^{-3}$	0.028	0.083	0.20
1700	$1.3\text{x}10^{-3}$	$4.7\text{x}10^{-3}$	0.017	0.052	0.14
1900	$6.9\text{x}10^{-4}$	$2.6\text{x}10^{-3}$	$9.5\text{x}10^{-3}$	0.032	0.091
2100	$3.7\text{x}10^{-4}$	$1.4\text{x}10^{-3}$	$5.3\text{x}10^{-3}$	0.018	0.057
2300	$2.0\text{x}10^{-4}$	$7.7\text{x}10^{-4}$	$2.9\text{x}10^{-3}$	0.010	0.035
2500	$9.3\text{x}10^{-5}$	$3.6\text{x}10^{-4}$	$1.4\text{x}10^{-3}$	$5.2\text{x}10^{-3}$	0.018

(W. Tsang, October 1984)

23,2 $CH_3O_2 + H_2 \rightarrow CH_3O_2H + H$

Comments and Recommendations

There are no direct measurements. We suggest a rate constant expression similar to $k(HO_2 + H_2) = 5\text{x}10^{-11}\exp(-13100/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. This is however only an order of magnitude estimate.

(W. Tsang, May 1983)

23,4 $CH_3O_2 + H \rightarrow CH_3O + OH$ (a)
$\rightarrow CH_2O + H_2O$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
Slemr, Warneck (1977)	250-300	$1\text{x}10^{17}$	$k_b/k_a \sim 5$	

Comments and Recommendations

The results of Slemr and Warneck are the only measurements on this system. The products can only be rationalized through formation of a hot adduct. However, the existing data on the methyl hydroperoxide decomposition reaction (Kirk, Can. J. Chem. 43, 2236 (1965)) do not appear to suggest the importance of (b). We believe that there are surface components in the measurement of Slemr and Warneck. It is suggested that a rate constant close to collisional be used for $k_a \sim 1.6\text{x}10^{-10}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. k_b is unimportant. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

References

Slemr, F., and Warneck, P., "Kinetics of the Reaction of Atomic Hydrogen with Methyl Hydroperoxide," Int. J. Chem. Kinet. 9, 267 (1977)

23,5 $CH_3O_2 + O \rightarrow CH_3O + O_2$

Comments and Recommendations

There are no measurements on this process. Since this is a very exothermic process and the O-OO bond is very weak an appropriate rate constant will be near collisional $\sim 6\text{x}10^{-11}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ with an uncertainty of about a factor of 3.

(W. Tsang, May 1983)

23,6 $CH_3O_2 + OH \rightarrow CH_3OH + O_2$

Comments and Recommendations

There are no experimental measurements. By analogy with the reaction of HO_2 + OH we suggest a collisional rate constant k ~ $1x10^{-10}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 5.

(W. Tsang, May 1983)

23,7 $CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
CODATA (1984) eval.	274-338		$7.7x10^{-14}exp(1300/T)$	5

Comments and Recommendations

The CODATA recommendation is based on the work of Cox and Tyndall (J. Chem. Soc., Faraday Trans. II 76, 153 (1980)). Presumably the process is analogous to the HO_2 self-reaction. The negative activation energy is indicative of an excited reactive intermediate. Extension of the rate expression to high temperatures and different pressures may lead to very different numbers.

(W. Tsang, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

23,8 $CH_3O_2 + H_2O_2 \rightarrow CH_3OOH + HO_2$

Comments and Recommendations

There are no direct measurements on this system. On the basis of analogous systems we estimate k ~ $4x10^{-12}exp(-5000/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 10.

(W. Tsang, May 1983)

23,10 $CH_3O_2 + CH_4 \rightarrow CH_3OOH + CH_3$

Comments and Recommendations

There are no direct measurements. It should be similar to $HO_2 + CH_4 \rightarrow CH_3 + H_2O_2$ for which we have estimated $k \sim 3x10^{-13}exp(-9300/T)cm^3molecule^{-1}s^{-1}$. The rate constant will have an uncertainty of a factor of 10.

(W. Tsang, May 1983)

23,11 $CH_3O_2 + C_2H_6 \rightarrow CH_3O_2H + C_2H_5$

Comments and Recommendations

There are no direct determinations. We recommend Walker's value for the analogous reaction (11,7) of $k(HO_2 + C_2H_6 \rightarrow C_2H_5 + H_2O_2) = 4.9x10^{-13}exp(-7520/T)cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 10.

(W. Tsang, May 1983)

23,12 $CH_3O_2 + HCHO \rightarrow CH_3O_2H + CHO$

Comments and Recommendations

There are no direct measurements. By analogy with the $HCHO + HO_2 \rightarrow H_2O_2 + CHO$ (12,7) process we recommend $k \sim 3.3x10^{-12}exp(-5870/T)cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 10.

(W. Tsang, May 1983)

23,15 $CH_3O_2 + HCO \rightarrow CH_3O + H + CO_2$

Comments and Recommendations

In the absence of any direct measurements we estimate the rate constant as close to collisional $k \sim 5x10^{-11}cm^3molecule^{-1}s^{-1}$ with products that would be expected from decomposition of a hot adduct. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

23,16 $CH_3O_2 + CH_3 \rightarrow 2CH_3O$

Comments and Recommendations

There are no direct measurements on this reaction. One expects a fast addition process with $k \sim 4\times10^{-11} cm^3 molecule^{-1} s^{-1}$ followed by decomposition of the hot adduct. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

23,17 $CH_3O_2 + C_2H_5 \rightarrow CH_3O + C_2H_5O$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with $k \sim 4\times10^{-11} cm^3 molecule^{-1} s^{-1}$ followed by decomposition of the hot adduct, with an uncertainty of a factor of 3.

(W. Tsang, May 1983)

23,19 $CH_3O_2 + C_2H_3 \rightarrow CH_3O + C_2H_3O$

Comments and Recommendations

In the absence of any experiments we expect that the mechanism will involve a fast combination process followed by decomposition of the hot adduct with a rate constant close to collisional $k \sim 4 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$. Uncertainty is a factor of 3.

(W. Tsang, May 1983)

23,21 $CH_3O_2 + C_2H \rightarrow CH_3O + HC_2O$

Comments and Recommendations

In the absence of experimental results we suggest that the important reaction will be addition followed by decomposition of the hot adduct. The rate will be close to collisional, $k \sim 4\times10^{-11} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 3. The stability of the HC≡C-O product is uncertain. If it decomposes, very reactive products may be formed.

(W. Tsang, May 1983)

23,22 $CH_3O_2 + CH_3CO \rightarrow CH_3 + CO_2 + CH_3O$

Comments and Recommendations

In the absence of experimental results we suggest that the main process will be combination at a near collisional rate of $k \sim 4\mathrm{x}10^{-11}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$ followed by rapid decomposition of the adduct. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

23,23 $2CH_3O_2 \rightarrow 2CH_3O + O_2$ (a)

$\rightarrow CH_3OH + CH_2O + O_2$ (b)

$\rightarrow CH_3O_2CH_3 + O_2$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$	Uncertainty factor
CODATA (1984) evaln.	298		$k_a = 1.3\mathrm{x}10^{-13}$	2
			$k_b = 2.1\mathrm{x}10^{-13}$	2
			$k_c < 3\mathrm{x}10^{-14}$	
Kirsch, Parkes (1981)	298-373	$2.5\mathrm{x}10^{19}$ O_2		
	333		$k_a/k_b = 0.85$	2
	373		$k_a/k_b = 1.3$	2

Comments and Recommendations

All rate constant measurements are near room temperature. In the absence of any other information the CODATA recommended rates should be used. However, the possibility of a temperature dependence introduces the possibility of larger uncertainties at higher temperatures.

(W. Tsang, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Kirsch, L. J., and Parkes, D. A., "Recombination of Tertiary Butyl Peroxy Radicals," J. Chem. Soc., Faraday Trans. I 77, 293 (1981)

24,1 $CH_3O + M \rightarrow HCHO + H + M$

Comments and Recommendations

There are no direct measurements on this reaction. L. Batt (Int. J. Chem. Kinet. 11, 977 (1979)) has suggested the high pressure unimolecular rate expression $10^{14.2}\exp(-13800/T)s^{-1}$. We have carried out RRKM calculations on this basis. The reaction under practically all conditions is in the 2nd order region. On a strong collision basis the rate expression is $k_o = 10^{2.5}(1/T)^{2.7}\exp(-15400/T)cm^3molecule^{-1}s^{-1}$ The small corrections to take into account deviation from bimolecular behavior can be found in Table A. Collision efficiency as a function of step size down and temperature can be found in Table B. We suggest the use of 450 cm^{-1} for Argon and N_2 and 1000 cm^{-1} for larger polyatomics. This leads to:

$k(N_2, 0) = 10^{13.81}T^{-6.65}\exp(-16740/T)$ and

$k(CH_3O, 0) = 10^{12.71}T^{-6.12}\exp(-16660/T)$

which for all practical purposes are applicable to conditions in the 0.1 to 10 atm range. The uncertainty is a factor of 4.

Table A. Values of $\log(k/k\infty)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
18.0	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01			
19.0	-0.09	-0.09	-0.08	-0.07	-0.07	-0.06	-0.05	-0.05	-0.04	-0.04	-0.04	-0.03
20.0	-0.48	-0.46	-0.43	-0.34	-0.34	-0.30	-0.26	-0.24	-0.20	-0.18	-0.16	-0.14
21.0	-1.30	-1.24	-1.13	-0.92	-0.90	-0.80	-0.70	-0.63	-0.56	-0.49	-0.44	-0.38

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.70	0.83
500	0.067	0.17	0.34	0.54	0.72
700	0.035	0.10	0.23	0.42	0.62
900	0.020	0.061	0.16	0.32	0.53
1100	0.012	0.031	0.11	0.24	0.44
1300	$7.4x10^{-3}$	0.025	0.075	0.19	0.36
1500	$4.7x10^{-3}$	0.017	0.052	0.14	0.29
1700	$3.1x10^{-3}$	0.011	0.036	0.10	0.23
1900	$2.0x10^{-3}$	$7.3x10^{-3}$	0.025	0.074	0.18
2100	$1.3x10^{-3}$	$4.9x10^{-3}$	0.017	0.054	0.14
2300	$8.7x10^{-3}$	$3.3x10^{-3}$	0.012	0.038	0.11
2500	$5.8x10^{-3}$	$2.2x10^{-3}$	$8x10^{-3}$	0.027	0.08

(W. Tsang, May 1983)

24,3 $CH_3O + O_2 \rightarrow HCHO + HO_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
CODATA (1984) evaln.	298-630		$1.1x10^{-13}exp(-1310/T)$	5
	298		$1.3x10^{-15}$	
NASA (1985) evaln.	200-300		$8.4x10^{-14}exp(-1200/T)$	
	298		$1.5x10^{-15}$	

Comments and Recommendations

The CODATA(1984) recommended value is accepted. It is based on the recent results of Gutman et al. (1982) over the temperature range 413 to 608 K. The room temperature value is very uncertain as is the value of E/R (±500 K).

(R. F. Hampson, May 1983)

References

CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

Gutman, D., and Sanders, N., and Butler, J. E., "Kinetics of the Reactions of Methoxy and Ethoxy Radicals with Oxygen," J. Phys. Chem. 86, 66 (1982)

NASA(1985). Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation No. 7, NASA Panel for Data Evaluation, JPL Publication 85-37 July 1985

24,4 $CH_3O + H \rightarrow HCHO + H_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Hoyermann, et al. (1981)	300	$3x10^{16}$	$3.3x10^{-11}$	3

Comments and Recommendations

This reaction was studied in a fast flow reactor, using mass spectrometric detection of isotopically labelled species. Its rate was determined relative to that for the reaction $C_2H_5 + H \rightarrow$ products. It was also shown that the direct abstraction reaction accounts for 75% of the total reaction with about 25% proceeding by complex formation to give an excited CH_3OH. Uncertainty is a factor of 3.

(R. F. Hampson, May 1983)

References

Hoyermann, K., Loftfield, N. S., Sievert, R., and Wagner, H. Gg., "Mechanisms and Rates of the Reactions of CH_3O and CH_2OH Radicals with H Atoms," Symp. Combust. 18, (Combustion Institute, Pittsburgh, Pa., 1981) 831

24,5 $CH_3O + O \rightarrow CH_2O + OH$

Comments and Recommendations

In the absence of any experimental data it is likely that this highly exothermic reaction (335 kJ mol^{-1}) proceeds at a rapid rate with $k \sim 1 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ and an uncertainty factor of 5.

(R. F. Hampson, May 1983)

24,6 $CH_3O + OH \rightarrow CH_2O + H_2O$

Comments and Recommendations

In the absence of any experimental data, it is likely that this highly exothermic reaction (405 kJ mol^{-1}) proceeds at a rapid rate with $k \sim 3x10^{-11} cm^3 molecule^{-1} s^{-1}$ and an uncertainty factor of 5.

(R. F. Hampson, May 1983)

24,7 $CH_3O + HO_2 \rightarrow CH_2O + H_2O_2$

Comments and Recommendations

In the absence of any experimental data we suggest using the rate for the analogous reaction 24,23 $CH_3O + CH_3O_2 \rightarrow CH_2O + CH_3OOH$ for which the preferred value $k = 5x10^{-13} cm^3 molecule^{-1} s^{-1}$ was given with an uncertainty of a factor of 10.

(R. F. Hampson, May 1983)

24,10 $CH_3O + CH_4 \rightarrow CH_3OH + CH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
$\log K_p = 1.26812 - 118.655/T - 69988/T^2 + 1.35384x10^7/T^3$				
Shaw, Thynne (1966)	455		$1.5x10^{-17}$	10

Comments and Recommendations

The value given here is based on the results of Shaw and Thynne and is a factor of 3 higher than their published value due to the use of more recent thermodynamic data in converting the measured value of the reverse rate constant. A calculation using the BSBL technique give $E_{act} = 37$ kJ mol^{-1} which when combined with this rate constant value, gives the Arrhenius expression $2.6x10^{-13} exp(-4450/T) cm^3 molecule^{-1} s^{-1}$. Uncertainty is a factor of 3.

(R. F. Hampson, May 1983)

References

Shaw, R., and Thynne, J. C. J., "Hydrogen and Deuterium Atom Abstraction from Methanol and Trideuteromethanol. Reaction of Methoxy Radical with Methane," Trans. Faraday Soc. 62, 104 (1966)

24,11 $CH_3O + C_2H_6 \rightarrow CH_3OH + C_2H_5$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Gray, et al. (1967) review			$4\times10^{-13}\exp(-3570/T)$	3

Comments and Recommendations

This value appears reasonable when compared with the expression derived for $CH_3O + CH_4$ (24,10). A BSBL calculation yields a value for the activation energy in good agreement with the above. Uncertainty is a factor of 3.
(R. F. Hampson, May 1983)

References

Gray, P., Shaw, R., and Thynne, J. C. J., "The Rate Constants of Alkoxyl Radical Reactions," Progr. React. Kinet. 4, 63 (1967)

24,12 $CH_3O + HCHO \rightarrow CH_3OH + HCO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
$\log K_p = 1.00014 + 3719.01/T - 58627/T^2 + 1.03026\times10^7/T^3$				
Gray, et al. (1967) review	323-408		$1.7\times10^{-13}\exp(-1500/T)$	3

Comments and Recommendations

The expression given by Gray, et al. is based on results of Hoare and Wellington obtained in a system where this reaction competes with the disproportionation of two CH_3O radicals. Uncertainty is a factor of 3.
(R. F. Hampson, May 1983)

References

Gray, P., Shaw, R., and Thynne, J. C. J., "The Rate Constants of Alkoxyl Radical Reactions," Progr. React. Kinet. 4, 63 (1967)
Hoare, D. E., and Wellington, C. A., "Reactions of t-Butoxy, Methoxy and Acetonyl Radicals," Symp. Combust. 8, (Combustion Institute, Baltimore, 1962) 472

24,14 $CH_3O + CO \rightarrow CH_3 + CO_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Lissi, et al. (1973)	396-426	$(4-110)x10^{17}$ CO	$2.6x10^{-11}exp(-5940/T)$	3
Sanders, et al. (1980)	298		$< 8x10^{-15}$	
Wiebe, Heicklen (1973)	298-423		$k/k(CH_3O+NO) = 5x10^{-4}$	

Comments and Recommendations

The recommended value is the expression reported by Lissi, et al. who monitored the rate of production of CO_2 from the thermal decomposition of dimethyl peroxide in the presence of CO. However because of the large discrepancy with the value which can be derived from the relative rate study of Wiebe and Heicklen (1973), the uncertainty must be taken to be at least a factor of 5. Sanders, et al. could not measure the rate and simply reported on upper limit based on technique sensitivity.

(R. F. Hampson, May 1983)

References

Lissi, E. A., Massiff, G., and Villa, A. E., "Oxidation of Carbon Monoxide by Methoxy-Radicals," J. Chem. Soc., Faraday Trans. I 69, 346 (1973)

Sanders, N., Butler, J. E., Pasternack, L. R., and McDonald, J. R., "CH_3O Production from 266 nm Photolysis of Methyl Nitrite and Reaction with NO," Chem. Phys. 48, 203 (1980)

Wiebe, H. A., and Heicklen, J., "Photolysis of Methyl Nitrite," J. Am. Chem. Soc. 95, 1 (1973)

24,15 $CH_3O + HCO \rightarrow CH_3OH + CO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Quee, Thynne (1967)	303	$1x10^{18}$ methyl formate	$2.3x10^{-10}$ (based on CH_3OH formation) $8x10^{-11}$ (based on CO formation)	3

Comments and Recommendations

On the basis of this work we suggest using the average of the values obtained by different methods, i.e. $1.5x10^{-10} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of least a factor of 3. The predominant path appears to be disproportionation to give the products shown.

(R. F. Hampson, May 1983)

References

Quee, M. J. Y., and Thynne, J. C. J., "Photolysis of Methyl Formate," Trans. Faraday Soc. 63, 1656 (1967)

24,16 $CH_3O + CH_3 \rightarrow CH_2O + CH_4$ (a)
$\rightarrow CH_3OCH_3$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Quee, Thynne (1966)	314-366	$(3-9)x10^{17}$ dimethyl carbonate	$k_a/k_b = 1.9±0.3$	1.2
Thynne, Gray (1963)	393-455	10^{17} dimethyl peroxide 10^{18} methyl formate	$k_a/k_b = 1.5±0.2$	1.2

Comments and Recommendations

Gray, Shaw and Thynne (1967) estimate the value of the combination rate constant $k_b \sim 2x10^{-11} cm^3 molecule^{-1} s^{-1}$ based on the combination rate of methyl radicals and of methoxy radicals. Using this rate and the ratio reported by Quee and Thynne, we suggest that the favored path is disproportionation with a rate constant of ~ $4x10^{-11} cm^3 molecule^{-1} s^{-1}$. Uncertainty is a factor of 5.

(R. F. Hampson, May 1983)

References

Gray, P., Shaw, R., and Thynne, J. C. J., "The Rate Constants of Alkoxyl Radical Reactions," Progr. React. Kinet. 4, 63 (1967)

Quee, M. J. Y., and Thynne, J. C. J., "Photolysis of Dimethyl Carbonate," Trans. Faraday Soc. 62, 3154 (1966)

Thynne, J. C. J., and Gray, P., "Methoxy-Radical-Induced Decomposition of Methyl Formate: Kinetics of Methoxyl and Methyl Radical Reactions," Trans. Faraday Soc. 59, 1149 (1963)

24,17 $CH_3O + C_2H_5 \rightarrow CH_2O + C_2H_6$

Comments and Recommendations

In the absence of any data for this reaction, we suggest using the value of the rate constant for the disproportionation of CH_3O with CH_3, i.e. $4x10^{-11} cm^3 molecule^{-1} s^{-1}$. Uncertainty is a factor of 5.

(R. F. Hampson, May 1983)

24,18 $CH_3O + C_2H_4 \rightarrow$ products

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Lissi, et al. (1975)	400	$(3\text{-}12)\times10^{18}$	4×10^{-17}	

Comments and Recommendations

The rate of this reaction was measured by a competitive technique and was converted to an absolute value of the rate constant using the value obtained previously (1973) by these authors for the rate of the reference reaction $CH_3O + CO \rightarrow CO_2 + CH_3$. The value given here is somewhat lower than the value published in the 1975 paper because of an error in the calculated value of the rate of the reference reaction from the parameters reported in the 1973 paper. The primary reaction at lower temperatures is addition. This will be reversed at higher temperatures. The addition product can also undergo 1,4-H-migration leading to HCHO and C_2H_5. Scaling of the results to an A-factor of $2 \times 10^{-13} cm^3 molecule^{-1}s^{-1}$ leads to the rate expression

$$k \approx 2\times10^{-13}\exp(-3400/T)cm^3molecule^{-1}s^{-1}$$

with an uncertainty of over a factor of 10 at high temperatures.

(R. F. Hampson, October 1984)

References

Lissi, E. A., Massiff, G., and Villa, A., "Addition of Methoxy Radicals to Olefins," Int. J. Chem. Kinet. 7, 625 (1975)

Lissi, E. A., Massiff, G., and Villa, A., "Oxidation of Carbon Monoxide by Methoxy-Radicals," J. Chem. Soc., Faraday Trans. I 69, 346 (1973)

24,19 $CH_3O + C_2H_3 \rightarrow CH_2O + C_2H_4$

Comments and Recommendations

In the absence of any data for this reaction, we suggest using the value of the rate constant for the disproportionation of CH_3O with CH_3, i.e. $4\times10^{-11}cm^3molecule^{-1}s^{-1}$. Uncertainty is a factor of 5.

(R. F. Hampson, May 1983)

24,20 $CH_3O + C_2H_2 \rightarrow$ products

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Lissi, et al. (1975)	400		$7x10^{-17}$ based on reported value of $k/k(CH_3O + C_2H_4) = 1.7$	

Comments and Recommendations

In this study the rate was measured by a competitive technique with the reference reaction being $CH_3O + C_2H_4 \rightarrow$ products. As discussed in data sheet for (24,18) this latter rate was measured relative to the rate of $CH_3O + CO \rightarrow CO_2 + CH_3$. Following the data sheet on $C_2H_4 + CH_3O$ (24,18) we note the possibility of addition, its reverse and 1,4-H-migration leading to $C_2H_3 + CH_2O$. The estimated rate expression is $k \sim 2x10^{-13}exp(-10000/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of 10 at higher temperatures.

(R. F. Hampson, May 1983)

References

Lissi, E. A., Massiff, G., and Villa, A., "Addition of Methoxy Radicals to Olefins," Int. J. Chem. Kinet. 7, 625 (1975)

24,21 $CH_3O + C_2H \rightarrow CH_2O + C_2H_2$

Comments and Recommendations

In the absence of any data for this reaction, we suggest using the value of the rate constant for the disproportionation of CH_3O with CH_3, i.e. $4x10^{-11}cm^3molecule^{-1}s^{-1}$. Uncertainty is a factor of 5.

(R. F. Hampson, May 1983)

24,22 $CH_3O + CH_3CO \rightarrow CH_3OH + CH_2CO$ (a)
$\rightarrow CH_2O + CH_3CHO$ (b)

Comments and Recommendations

In the absence of any experimental data on this reaction, we believe that these radicals will disproportionate rapidly. Since paths a and b are equally exothermic ~ 250 kJ mol^{-1} we suggest using the values $k_a = k_b = 1x10^{-11} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 10.

(R. F. Hampson, May 1983)

24,23 $CH_3O + CH_3O_2 \rightarrow CH_2O + CH_3OOH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Dever, Calvert (1962)	298	$2.4x10^{19}$ O_2 $1x10^{16}$ azomethane	$5x10^{-13}$	10
Heicklen, Johnston (1962)	298	$(3-30)x10^{16}$ O_2 $(1-10)x10^{16}$ CH_3I	$5x10^{-13}$	10

Comments and Recommendations

Dever and Calvert (1962) studied the photooxidation of azomethane by long path infrared spectrometry. The value shown above is derived from the reported value of $(k_a \times (2k_b)^{1/2})/k$ where k_a refers to the reaction $CH_3O + CH_2O \rightarrow CH_3OH + HCO$ and k_b, the reaction $2CH_3O_2 \rightarrow 2CH_3O + O_2$. The numerical value of this expression given in that paper appears to be incorrectly derived and has been corrected here. Heicklen and Johnston studied the photooxidation of methyl iodide by mass spectrometry. The value shown above is derived from the reported value of $k/(k_b x k_c)^{1/2} = 0.14$ where k_c refers to $2CH_3O \rightarrow CH_3OH + CH_2O$ and k_b is as given above. Both systems are complex photochemical systems, and therefore a large uncertainty (a factor of 10) should be associated with the preferred value of $5x10^{-13}$ $cm^3 molecule^{-1} s^{-1}$.

(R. F. Hampson, May 1983)

References

Dever, D. F., and Calvert, J. G., "Rate Studies of the Oxidation of Methyl Radicals in Oxygen-rich Media at 25 C," J. Am. Chem. Soc. 84, 1362 (1962)

Heicklen, J., and Johnston, H. S., "Photochemical Oxidations. II. Methyl Iodide," J. Am. Chem. Soc. 84, 4030 (1962)

25,1 $^1CH_2 + N_2 \rightarrow {}^3CH_2 + N_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Langford, et al. (1983)	298	(3-30)x10^{17} N_2	11x10^{-12}	1.1
Ashfold, et al. (1981)	298	(6-60)x10^{16} N_2	8.8x10^{-12}	1.3
Laufer (1981) review	298		9x10^{-13}	

Comments and Recommendations

The results reported by Ashfold et al. (1981) were obtained using IR laser multiphoton dissociation and time resolved laser induced fluorescence. The results of Langford et al. (1983) were obtained using cw laser resonance absorption. These recent results are in good agreement and are an order of magnitude faster than the earlier results. The preferred value is the average of the two recent results (1.0x10^{-11} cm^{3}molecule^{-1}s^{-1}). Uncertainty is a factor of 1.3. Although the values reported are for the total removal rate of singlet CH_2, they probably refer to the singlet-triplet intersystem crossing, since the pressure range was much too low for third order recombination to be important. Braun et al. (1970) estimated the quenching half-pressure for CH_2N_2 formation to be 400 torr.

(R. F. Hampson, May 1984)

References

Ashfold, M. N. R., Fullstone, M. A., Hancock, G., and Ketley, G. W., "Singlet Methylene Kinetics: Direct Measurements of Removal Rates of a^1A_1 and b^1B_1 CH_2 and CD_2," Chem. Phys. 55, 245 (1981)

Braun, W., Bass, A. M., and Pilling, M., "Flash Photolysis of Ketene and Diazomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene," J. Chem. Phys. 52, 5131 (1970)

Langford, A. O., Petek, H., and Moore, C. B., "Collisional Removal of $CH_2(^1A_1)$: Absolute Rate Constants for Atomic and Molecular Collisional Partners at 295 K," J. Chem. Phys. 78, 6650 (1983)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

25,2 $^1CH_2 + H_2 \rightarrow CH_3 + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Langford, et al. (1983)	298	$(3-30)x10^{17}$ N_2	$1.05x10^{-10}$	1.05
Ashfold, et al. (1981)	298	$(6-60)x10^{16}$ N_2	$1.3x10^{-10}$	1.07
Laufer (1981) review	298		$7x10^{-12}$	

Comments and Recommendations

The recommended value of $1.2x10^{-10}$ $cm^3molecule^{-1}s^{-1}$ is taken to be the average of the recent results of Langford et al. (1983) and Ashfold et al. (1981). The uncertainty is a factor of 1.3. The value given in Laufer's review is based on results of flash photolysis-kinetic spectroscopy experiments reported by Braun et al. (1970). Although these are for the total removal rate of singlet CH_2, Braun et al. have shown that reaction to produce methyl radicals accounts for more than 80 percent of the removal rate. (R. F. Hampson, May 1984)

References

Ashfold, M. N. R., Fullstone, M. A., Hancock, G., and Ketley, G. W., "Singlet Methylene Kinetics: Direct Measurements of Removal Rates of a^1A_1 and b^1B_1 CH_2 and CD_2," Chem. Phys. 55, 245 (1981)

Braun, W., Bass, A. M., and Pilling, M., "Flash Photolysis of Ketene and Diazomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene," J. Chem. Phys. 52, 5131 (1970)

Langford, A. O., Petek, H., and Moore, C. B., "Collisional Removal of $CH_2(^1A_1)$: Absolute Rate Constants for Atomic and Molecular Collisional Partners at 295 K," J. Chem. Phys. 78, 6650 (1983)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

25,3 $^1CH_2 + O_2 \rightarrow H + CO + OH$ (a)
$\rightarrow H_2 + CO$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Langford, et al. (1983)	298	$(3-30)x10^{17}$ N_2	$7.4x10^{-11}$	1.07
Ashfold, et al. (1981)	298	$(6-60)x10^{17}$	$3.0x10^{-11}$	1.13
Laufer (1981) review	298		$< 3x10^{-11}$	

Comments and Recommendations

The recommended value of $5.2\times10^{-11}cm^3molecule^{-1}s^{-1}$ is taken to be the average of the recent results of Langford et al. (1983) and Ashfold et al. (1981). Uncertainty is a factor of 1.6. In agreement with these results, Rowland et al. (1972) report that this reaction proceeds with a collision efficiency of about 0.1. The upper limit given in Laufer's review is based on flash photolysis-gas chromatography results of Laufer and Bass(1974). It is proportional to the value used for the rate of deactivation by helium which the authors took from Braun et al. (1970). The reported value should be increased by an order of magnitude on the basis of new results for the reference rate reported by Ashfold et al. (1981) and Langford et al. (1983). Shaub et al. (1981) suggest that the relative importance of the two reaction channels is the same as for the corresponding reaction of triplet methylene, where 70% of the CO is formed in the radical production path (a) and 30% is formed in the molecular elimination channel (b).

(R. F. Hampson, May 1984)

References

Ashfold, M. N. R., Fullstone, M. A., Hancock, G., and Ketley, G. W., "Singlet Methylene Kinetics: Direct Measurements of Removal Rates of a^1A_1 and b^1B_1 CH_2 and CD_2," Chem. Phys. 55, 245 (1981)

Braun, W., Bass, A. M., and Pilling, M., "Flash Photolysis of Ketene and Diazaomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene," J. Chem. Phys. 52, 5131 (1970)

Langford, A. O., Petek, H., and Moore, C. B., "Collisional Removal of $CH_2(^1A_1)$: Absolute Rate Constants for Atomic and Molecular Collisional Partners at 295 K," J. Chem. Phys. 78, 6650 (1983)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. H., "Rate Constants for Reactions of Methylene with Carbon Monoxide, Oxygen, Nitric Oxide, and Acetylene," J. Phys. Chem. 78,, 1344 (1974)

Rowland, F. S., Lee, P. S.-T., Montague, D. C., and Russell, R. L., "Tracer Studies of the Reactions of Singlet and Triplet Methylene in the Gas Phase," Faraday Discuss. Chem. Soc. 53, 111 (1972)

Shaub, W. M., Hsu, D. S. Y., Burks, T. L., and Lin, M. C., "Dynamics and Mechanisms of CO Production from the Reactions of CH_2 Radicals with $O(^3P)$ and O_2," Symp. Combust. 18, (Combustion Institute, Pittsburgh, 1981) 811

25,4 $^1CH_2 + H \rightarrow CH + H_2$

Comments and Recommendations

In the absence of experimental data, it is suggested that this reaction, which is exothermic by 29 kJ mol^{-1} proceeds at a near collisional rate of $\sim 5\times10^{-11}$ $cm^3molecule^{-1}s^{-1}$. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,5 $^1CH_2 + O \rightarrow CO + 2H$ (a)

$\rightarrow CO + H_2$ (b)

Comments and Recommendations

The recommended value for this rate constant is 5 x $10^{-11}cm^3molecule^{-1}s^{-1}$ based on analogy with the rate of the slightly less exothermic reaction of triplet methylene. Shaub, et al. from a study of the vibrational energy distribution of the CO produced concluded that, as in the case of triplet methylene, the two reaction channels shown are equally important. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

References

Shaub, W. M., Hsu, D. S. Y., Burks, T. L., and Lin, M. C., "Dynamics and Mechanisms of CO Production from the Reactions of CH_2 Radicals with $O(^3P)$ and O_2," Symp. Combust. 18, (Combustion Institute, Pittsburgh, 1981) 811

25,6 $^1CH_2 + OH \rightarrow HCHO + H$

Comments and Recommendations

In the absence of experimental data it is suggested that the reaction proceeds at a near collisional rate of ~ 5 x 10^{-11} $cm^3molecule^{-1}s^{-1}$ to form an excited complex which dissociates to HCHO + H. The overall reaction is highly exothermic (~ 360 kJ mol^{-1}). Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,7 $^1CH_2 + HO_2 \rightarrow HCHO + OH$

Comments and Recommendations

In the absence of experimental data it is suggested that this reaction proceeds at a near collisional rate of ~ 5 x 10^{-11} $cm^3molecule^{-1}s^{-1}$ to form an excited complex which dissociates to HCHO + OH. The overall reaction is highly exothermic (~ 510 kJ mol^{-1}).

(R. F. Hampson, May 1984)

25,8 $^1CH_2 + H_2O_2 \rightarrow CH_3O + OH$

Comments and Recommendations

There are no experimental data on this reaction. In contrast to the reaction of $^1CH_2$ with H_2O where the initially formed adduct does not have sufficient energy to decompose to products, here the CH_3OOH adduct can decompose; the overall reaction is exothermic by 226 kJ mol^{-1}. The rate is expected to be fast ($k \sim 5 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$) by comparison with other insertion reactions of $^1CH_2$. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,9 $^1CH_2 + H \rightarrow CH + H_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Hatakeyama, et al. (1981)	298	2.5×10^{19} N_2	$\sim 3 \times 10^{-12}$	

Comments and Recommendations

The results of Hatekeyama were obtained in a competitive system with the reaction $^1CH_2 + CH_2N_2 \rightarrow C_2H_4 + N_2$. Products yields of CH_3OH and C_2H_4 were measured. This value is based upon a literature value of $3 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ for the reference reaction. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

References

Hatakeyama, S., Bandow, H., Okuda, M., and Akimoto, H., "Reaction of CH_2OO and $CH_2(^1A_1)$ with H_2O in the Gas Phase," J. Phys. Chem. 85, 2249 (1981)

25,10 $^1CH_2 + CH_4 \rightarrow C_2H_6^* \rightarrow 2CH_3$ (a)
$\rightarrow {}^3CH_2 + CH_4$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Langford, et al. (1983)	298	$(3\text{-}30) \times 10^{17}$ CH_4	$k_{a+b} = 7.0 \times 10^{-11}$	1.05
Ashfold et al. (1981)	298	$(6\text{-}60) \times 10^{16}$ CH_4	$k_{a+b} = 7.3 \times 10^{-11}$	1.10
Laufer (1981) review	298		$k_a = 1.9 \times 10^{-12}$ $k_b = 1.6 \times 10^{-12}$	

Comments and Recommendations

The recommended value of 7.1×10^{-11} $cm^3molecule^{-1}s^{-1}$ is taken as the average of the recent results of Langford et al. (1983) and Ashfold et al. (1981). It is likely that channel (a) predominates. The values given in Laufer's review are based on results of flash photolysis-kinetic spectroscopy experiments reported by Braun et al. (1970). The value of k_a is the low pressure value, with the half-pressure for stabilization of the excited ethane adduct being about 1 atmosphere. Uncertainty is a factor of 1.5. (R. F. Hampson, May 1984)

References

Ashfold, M. N. R., Fullstone, M. A., Hancock, G., and Ketley, G. W., "Singlet Methylene Kinetics: Direct Measurements of Removal Rates of a^1A_1 and b^1B_1 CH_2 and CD_2," Chem. Phys. 55, 245 (1981)

Braun, W., Bass, A. M., and Pilling, M., "Flash Photolysis of Ketene and Diazomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene," J. Chem. Phys. 52, 5131 (1970)

Langford, A. O., Petek, H., and Moore, C. B., "Collisional Removal of $CH_2(^1A_1)$: Absolute Rate Constants for Atomic and Molecular Collisional Partners at 295 K," J. Chem. Phys. 78, 6650 (1983)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

25,11 $^1CH_2 + C_2H_6 \rightarrow C_3H_8^* \rightarrow CH_3 + C_2H_5$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Langford, et al. (1983)	298	$(3-30)\times10^{17}$ C_2H_6	1.9×10^{-10}	1.1
Laufer (1981) review	298		4.5×10^{-12}	

Comments and Recommendations

The recommended value is the recent result by Langford et al. (1983). It is from a body of absolute rate data which is in good agreement with the independent body of absolute rate data in Ashfold et al. (1981). The value cited from Laufer's review is the average of two values given there. One is from relative insertion rates reported by Halberstadt and Crump (1972) and the other is from the relative reactivities reported by Hase and Simons (1971). Both relative rates were normalized to the value of Braun et al. (1970) for the rate of insertion into methane ($1.9\times10^{-12}cm^3molecule^{-1}s^{-1}$). If these relative rates are normalized to the rate of the reference reaction given in this evaluation, the resulting rate for insertion into ethane is in good agreement with

the very recent absolute value given above. Unvertainty is a factor of 2.
(R. F. Hampson, May 1984)

References

Ashfold, M. N. R., Fullstone, M. A., Hancock, G., and Ketley, G. W., "Singlet Methylene Kinetics: Direct Measurements of Removal Rates of a^1A_1 and b^1B_1 CH_2 and CD_2," Chem. Phys. 55, 245 (1981)

Braun, W., Bass, A. M., and Pilling, M., "Flash Photolysis of Ketene and Diazomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene," J. Chem. Phys. 52, 5131 (1970)

Halberstadt, M. L., and Crump, J., "Insertion of Methylene into the Carbon-Hydrogen Bonds of the C_1 to C_4 Alkanes," J. Photochem. 1, 295 (1972/73)

Hase, W. L., and Simons, J. W., "Excitation Energies of Chemically Activated Isobutane and Neopentane and the Correlation of Their Decomposition Rates with Radical Recombination Rates," J. Chem. Phys. 54, 1277 (1971)

Langford, A. O., Petek, H., and Moore, C. B., "Collisional Removal of $CH_2(^1A_1)$: Absolute Rate Constants for Atomic and Molecular Collisional Partners at 295 K," J. Chem. Phys. 78, 6650 (1983)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

25,12 $^1CH_2 + H_2CO \rightarrow CH_3 + HCO$

Comments and Recommendations

By analogy with the rate of the reaction of $^1CH_2$ with CH_4 it is estimated that $^1CH_2$ inserts into the C-H bond of H_2CO with a rate of ~ $7\times10^{-11}cm^3molecule^{-1}s^{-1}$ to give a highly excited CH_3CHO species which decomposes to CH_3 + HCO. A similar rate is assumed for the deactivation process, also by analogy with $^1CH_2 + CH_4$. Uncertainty is a factor of 3.
(R. F. Hampson, May 1984)

25,13 $^1CH_2 + CO_2 \rightarrow H_2CO + CO$

Comments and Recommendations

There are no experimental data on the rate or mechanism of this reaction. It is expected to be significantly faster than the corresponding reaction of the triplet; and there also exists the possibility of quenching of the singlet methylene. An estimate to be used with caution would be an overall rate constant of $5\times10^{-12}cm^3molecule^{-1}s^{-1}$ with an equal probability for chemical reaction or quenching of the singlet methylene. Uncertainty is a factor of 5.
(R. F. Hampson, May 1984)

25,14 $^1CH_2 + CO \rightarrow$ products

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Langford, et al. (1983)	298	(3-30)x10^{17} CO	4.9x10^{-11}	1.1
Ashfold, et al. (1981)	298	(3-30)x10^{16} CO	5.6x10^{-11}	1.1
Laufer (1981) review	298		< 9x10^{-12}	

Comments and Recommendations

The recommended value of 5.2x10^{-11} cm^{3}molecule^{-1}s^{-1} is taken as the average of the recent results of Langford et al. (1983) and Ashfold et al. (1981). The upper limit given in Laufer's review is proportional to the value used for the rate of deactivation by helium which value was taken from Braun et al. (1970). When the reported value is adjusted on the basis of new results for the reference rate, it is consistent with the two recent absolute values. Uncertainty is a factor of 1.4.

(R. F. Hampson, May 1984)

References

Ashfold, M. N. R., Fullstone, M. A., Hancock, G., and Ketley, G. W., "Singlet Methylene Kinetics: Direct Measurements of Removal Rates of a^1A_1 and b^1B_1 CH_2 and CD_2," Chem. Phys. 55, 245 (1981)

Braun, W., Bass, A. M., and Pilling, M., "Flash Photolysis of Ketene and Diazomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene," J. Chem. Phys. 52, 5131 (1970)

Langford, A. O., Petek, H., and Moore, C. B., "Collisional Removal of $CH_2(^1A_1)$: Absolute Rate Constants for Atomic and Molecular Collisional Partners at 295 K," J. Chem. Phys. 78, 6650 (1983)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. M., "Rate Constants for Reactions of Methylene with Carbon Monoxide, Oxygen, Nitric Oxide, and Acetylene," J. Phys. Chem. 78, 1344 (1974)

25,15 $^1CH_2 + HCO \rightarrow CH_3 + CO$

Comments and Recommendations

Since $^1CH_2$ is known to insert rapidly into C-H bonds, this reaction probably proceeds at near collisional rate (k ~ 3x10^{-11}cm^{3}molecule^{-1}s^{-1}) to give a highly excited CH_3CO species which rapidly decomposes to CH_3 + CO. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,16 $^1CH_2 + CH_3 \rightarrow C_2H_4 + H$

Comments and Recommendations

There are no experimental data on the rate of this reaction. Since $^1CH_2$ is known to insert rapidly into C-H bonds, this reaction probably proceeds at near collisional rate ($k \sim 3\times10^{-11} cm^3 molecule^{-1} s^{-1}$) to give a highly excited C_2H_5 species with 440 kJ mol^{-1} internal energy, which rapidly decomposes to C_2H_4 + H. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,17 $^1CH_2 + C_2H_5 \rightarrow C_2H_4 + CH_3$ (a)
$\rightarrow C_3H_6 + H$ (b)

Comments and Recommendations

There are no experimental data on this reaction. Since $^1CH_2$ is known to insert rapidly into C-H bonds, this reaction probably proceeds at a near collisional rate ($k \sim 3\times10^{-11} cm^3 molecule^{-1} s^{-1}$) to give a highly excited C_3H_7 species with ~ 420 kJ mol^{-1} internal energy. This excited species will rapidly decompose by the two paths indicated with a suggested branching ratio of close to unity. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,18 $^1CH_2 + C_2H_4 \rightarrow C_3H_6$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Langford, et al. (1983)	298	$(3\text{-}30)\times10^{17}$ C_2H_4	1.5×10^{-10}	1.4

Comments and Recommendations

This is the only reported absolute value for this rate constant. It is from a body of absolute rate data which is in good agreement with the independent body of absolute rate data in Ashfold et al. (1981). The available relative data have been considered by Laufer in his recent review. The major path is addition to the double bond to form vibrationally excited cyclopropane which isomerizes to propylene. Uncertainty is a factor of 2.

(R. F. Hampson, May 1984)

References

Ashfold, M. N. R., Fullstone, M. A., Hancock, G., and Ketley, G. W., "Singlet Methylene Kinetics: Direct Measurements of Removal Rates of a^1A_1 and b^1B_1 CH_2 and CD_2," Chem. Phys. 55, 245 (1981)

Langford, A. O., Petek, H., and Moore, C. B., "Collisional Removal of $CH_2(^1A_1)$: Absolute Rate Constants for Atomic and Molecular Collisional Partners at 295 K," J. Chem. Phys. 78, 6650 (1983)

Laufer, A. H., "Kinetics of Gas Phase Reaction of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

25,19 $^1CH_2 + C_2H_3 \rightarrow C_2H_2 + CH_3$

Comments and Recommendations

Since $^1CH_2$ is known to insert rapidly into C-H bonds, this reaction probably proceeds at a near collisional rate ($k \sim 3x10^{-11} cm^3 molecule^{-1}s^{-1}$) to give an excited C_3H_5 species which rapidly decomposes to $C_2H_2 + CH_3$. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,20 $^1CH_2 + C_2H_2 \rightarrow C_3H_4$

Comments and Recommendations

There have been no direct measurements of the rate of this reaction. By analogy with the reaction of $^1CH_2$ with C_2H_4 this reaction is expected to be a fast reaction ($k \sim 1x10^{-10} cm^3 molecule^{-1}s^{-1}$) and the major pathway is expected to involve addition to the multiple bond and subsequent isomerization to yield methylacetylene. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,21 $^1CH_2 + C_2H \rightarrow C_2H_2 + CH$

Comments and Recommendations

Although there are no data on the rate of this reaction. it probably proceeds by an abstraction mechanism to give the products indicated with a rate constant of $\sim 3x10^{-11} cm^3 molecule^{-1}s^{-1}$. The product of a possible insertion reaction by $^1CH_2$ would be C_2CH_3. However, breakage of the C-C bond to give $C_2 + CH_3$ would constitute an endothermic overall pathway. It would be thermodynamically possible for the insertion adduct to be stabilized if it rearranges to the propargyl radical, $HCCCH_2$. We cannot estimate a branching ratio. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,22 $^1CH_2 + CH_3CO \rightarrow CH_3 + CH_2CO$

Comments and Recommendations

Since $^1CH_2$ is known to insert rapidly into C-H bonds this reaction probably proceeds at near collisional rate ($k \sim 3\times10^{-11}cm^3molecule^{-1}s^{-1}$) to give an excited CH_3CH_2CO species which rapidly decomposes to methyl radical + ketene. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,23 $^1CH_2 + CH_3O_2 \rightarrow C_2H_5 + O_2$

Comments and Recommendations

There are no data on this reaction. Since $^1CH_2$ is known to insert rapidly into C-H bonds, this reaction probably proceeds at near collisional rate ($k \sim 3\times10^{-11}cm^3molecule^{-1}s^{-1}$) to give a highly excited $C_2H_5O_2$ species with ~ 455 kJ mol^{-1} internal energy which rapidly decomposes to $C_2H_5 + O_2$. Uncertainty factor is 3.

(R. F. Hampson, May 1984)

25,24 $^1CH_2 + CH_3O \rightarrow CH_3 + CH_2O$

Comments and Recommendations

There are no experimental data on the rate of this reaction. Since $^1CH_2$ is known to insert rapidly into C-H bonds, this reaction probably proceeds at a near collisional rate ($k \sim 3\times10^{-11}cm^3molecule^{-1}s^{-1}$) to give a highly excited C_2H_5O species with 435 kJ mol^{-1} internal energy which rapidly decomposes to $CH_3 + CH_2O$. Uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

25,25 $^1CH_2 + {}^1CH_2 \rightarrow$ products

Comments and Recommendations

There are no experimental data on the rate on this reaction. It is expected to proceed rapidly ($k \sim 5\times10^{-11}cm^3molecule^{-1}s^{-1}$) to yield the same products as the reaction of two triplet species i.e. C_2H_2 and H_2 or 2H. The uncertainty factor is 5.

(R. F. Hampson, May 1984)

26,1 $^3CH_2 + N_2 \rightarrow$ products

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$< 1x10^{-16}$	

Comments and Recommendations

The recommended value is the upper limit recommended in Laufer's review and is based on results of flash photolysis-gas chromatography experiments reported by Laufer and Bass (1978)

(R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. M., "A New Channel for the Formation of Hydrogen Cyanide in CH_3-N_2 Systems," Combust. Flame 32, 215 (1978)

26,2 $^3CH_2 + H_2 \rightarrow CH_3 + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$< 5x10^{-15}$	

Comments and Recommendations

The recommended value is the upper limit given in Laufer's review and is based on the upper limit reported by Pilling and Robertson (1977) and a less sensitive upper limit reported by Braun et al. (1979).

(R. F. Hampson, May 1984)

References

Braun, W., Bass, A. M., and Pilling, M., "Flash Photolysis of Ketene and Diazomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene," J. Chem. Phys. 52, 5131 (1970)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Pilling, M. J., and Robertson, J. A., "Flash Photolysis of Ketene. Photolysis Mechanism and Rate Constants for Singlet and Triplet Methylene," J. Chem. Soc., Faraday Trans. I 73, 968 (1977)

26,3 $^{3}CH_2 + O_2 \rightarrow H + CO + OH$ (a)
$\rightarrow H_2O + CO$ (b)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3 molecule^{-1} s^{-1}$	factor
Bohland, et al. (1984)	298	$5x10^{16}$ He	$3.3x10^{-12}$	1.2
Laufer (1981) review	298		$1.4x10^{-12}$	
Vinckier, Debruyn	295-573		$2.2x10^{-11} exp(-755/T)$	
(1979)	298		$1.7x10^{-12}$	

Comments and Recommendations

The recommended value is that given in Laufer's review (corrected value) and is based on results of flash photolysis-gas chromatography experiments reported by Laufer and Bass (1974) and by Pilling and Robertson (1977). The only temperature dependent study is that of Vinckier and Debruyn (1979). These results by a completely different technique are in good agreement with the earlier results at room temperature. Reaction proceeds by addition to form a diradical intermediate which isomerizes to a highly excited HCOOH species which then decomposes.

From an analysis of the CO product vibrational energy distribution, Shaub et al. (1981) concluded that 70% of the CO is formed in the radical producing path (a) and 30% is formed in the molecular elimination channel (b). The mechanism of this reaction in a matrix has been studied by Lee and Pimentel (1981). Uncertainty in derived values of k_a and k_b is a factor of 2.
(R. F. Hampson, October 1984)

References

Bohland, T., Temps, F., and Wagner, H. Gg., "Direct Determination of the Rate Constant for the Reaction $CH_2 + O_2$ with a LMR Spectrometer," Ber. Bunsenges. Phys. Chem. 88, 455 (1984)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. M., "Rate Constants for Reactions of Methylene with Carbon Monoxide, Oxygen, Nitric Oxide, and Acetylene," J. Phys. Chem. 78, 1344 (1974)

Lee, Y.-P., and Pimentel, G. C., "Formic Acid Chemiluminescence from Cryogenic Reaction between Triplet Methylene and Oxygen," J. Chem. Phys. 74, 4851 (1981)

Pilling, M. J., and Robertson, J. A., "Flash Photolysis of Ketene. Photolysis Mechanism and Rate Constants for Singlet and Triplet Methylene," J. Chem. Soc., Faraday Trans. I 73, 968 (1977)

Shaub, W. M., Hsu, D. S. Y., Burks, T. L., and Lin, M. C., "Dynamics and Mechanisms of CO Production from the Reactions of CH_2 Radicals with $O(^3P)$ and O_2." Symp. Combust. 18, (Combustion Institute, Pittsburgh, 1981) 811

Vinckier, C., and Debruyn, W., "Temperature Dependence of the Reactions of Methylene with Oxygen Atoms, Oxygen, and Nitric Oxide," J. Phys. Chem. 83, 2057 (1979)

26,4 $^3CH_2 + H \rightarrow CH + H_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Bohland, Temps (1984)	298	$5x10^{16}$ He	$2.7x10^{-10}$	

Comments and Recommendations

These results are in accord with fast reactions of H atoms with organic radicals. In the present case this is followed by rapid decomposition of the adduct. Uncertainty is a factor of 2. (R. F. Hampson, October 1984)

References

Bohland, T., and Temps, F., "Direct Determination of the Rate Constants for the Reaction $CH_2 + H \rightarrow CH + H_2$," Ber. Bunsenges. Physik. Chem. 88, 459 (1984)

26,5 $^3CH_2 + O \rightarrow CO + 2H$ (a)
$\rightarrow CO + H_2$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$1.9x10^{-11}$	

Comments and Recommendations

The recommended value is that given in Laufer's review and is based on relative measurements in discharge flow experiments which report the ratio $k/k(^3CH_2 + C_2H_2) = 3.1 \pm 0.2$. This ratio is combined with the value of $k(^3CH_2 + C_2H_2) = 6x10^{-12}cm^3molecule^{-1}s^{-1}$ (see data sheet for reaction (26,20)) to give the above value. Vinckier and Debruyn report zero activation energy over the temperature range 290 to 600 K. Schaub et al. studied the vibrational energy distribution of the CO formed. They concluded that CO is produced via the two reaction channels shown above, and that both channels are equally important. The observed CO population inversion results mainly from the molecular elimination channel (b) which is exothermic by 745 kJ mol^{-1}. CO is observed to be vibrationally excited up to a maximum of $v = 17$. Uncertainty in derived values of k_a and k_b is a factor of 2. (R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Shaub, W. M., Hsu, D. S. Y., Burks, T. L., and Lin, M. C., "Dynamics and Mechanisms of CO Production from the Reactions of CH_2 Radicals with $O(^3P)$ and O_2," Symp. Combust. 18 (Combustion Institute, Pittsburgh, 1981) 811

Vinckier, C., and Debruyn, W., "Temperature Dependence of the Reactions of Methylene with Oxygen Atoms, Oxygen, and Nitric Oxide," J. Phys. Chem. 83, 2057 (1979)

26,6 $^3CH_2 + OH \rightarrow HCHO + H$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with k ~ $3x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3. The overall reaction is endothermic by 322 kJ mol^{-1}. A second possible reaction channel to give $CH_3 + O(^3P)$ is slightly exothermic.

(R. F. Hampson, May 1984)

26,7 $^3CH_2 + HO_2 \rightarrow HCHO + OH$ (a)

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with an overall rate constant k ~ $3x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

26,8 $^3CH_2 + H_2O_2 \rightarrow CH_3 + HO_2$

Comments and Recommendations

In the absence of direct measurements, we estimate the rate of this reaction to be quite slow ($k < 1x10^{-14}cm^3molecule^{-1}s^{-1}$) on the basis of triplet methylene's inertness towards H atom abstraction.

(R. F. Hampson, May 1984)

26,9 $^3CH_2 + H_2O \rightarrow CH_3 + OH$

Comments and Recommendations

This reaction is endothermic and cannot be of any importance in combustion systems. A conservative upper limit would be to set $k < 1x10^{-16}cm^3molecule^{-1}s^{-1}$ on the basis of triplet methylene's inertness towards H atom abstraction and consideration of the energetics of this reaction.

(R. F. Hampson, May 1984)

26,10 $^3CH_2 + CH_4 \rightarrow CH_3 + CH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$< 3x10^{-19}$	

Comments and Recommendations

The recommended value is that given in Laufer's review and is based on results of a low-intensity photolysis study of the CH_2CO-CH_4 system (Lee et al. (1970)).
(R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Lee, P. S. T., Russell, R. L., and Rowland, F. S., "The Reactions of Triplet Methylene with Alkyl Radicals in Ordinary Photolysis Systems," Chem. Comm., 18 (1970)

26,11 $^3CH_2 + C_2H_6 \rightarrow$ products

Comments and Recommendations

By analogy with the reaction $^3CH_2 + CH_4$ (see preceding data sheet) it is expected that an upper limit of $3x10^{-19} cm^3 molecule^{-1} s^{-1}$ is appropriate for this rate constant.
(R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

26,12 $^3CH_2 + HCHO \rightarrow CH_3 + HCO$

Comments and Recommendations

In the absence of direct measurements, we estimate the rate of this reaction to be quite slow ($k < 1x10^{-14} cm^3 molecule^{-1} s^{-1}$) on the basis of triplet methylene's inertness towards H atom abstraction.
(R. F. Hampson, May 1984)

26,13 $^3CH_2 + CO_2 \rightarrow HCHO + CO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$3.9x10^{-14}$	

Comments and Recommendations

The recommended value is that given in Laufer's review and is based on results of experiments reported by Laufer and Bass (1977) using flash photolysis in conjunction with gas chromatography and kinetic spectroscopy. They observed approximately 15% of the CO produced to be vibrationally excited to at least v'=2. Uncertainty is a factor of 1.6.

(R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. M., "Reaction Between Triplet Methylene and CO_2: Rate Constant Determination," Chem. Phys. Lett. 46, 151 (1977)

26,14 $^3CH_2 + CO \rightarrow CH_2CO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$< 1x10^{-15}$	

Comments and Recommendations

The recommended value is the upper limit given in Laufer's review and is based on results of flash photolysis-gas chromatography experiments reported by Laufer and Bass (1974) and Pilling and Robertson (1977) and tracer studies by Montague and Rowland (1971).

(R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. M., "Rate Constants for Reactions of Methylene with Carbon Monoxide, Oxygen, Nitric Oxide, and Acetylene," J. Phys. Chem. 78, 1344 (1974)

Montague, D. C., and Rowland, F. S, "Oxirene Intermediate in the Reaction of Singlet Methylene with Carbon Monoxide," J. Am. Chem. Soc. 93, 5381 (1971)

Pilling, M. J., and Robertson, J. A., "Flash Photolysis of Ketene. Photolysis Mechanism and Rate Constants for Singlet and Triplet Methylene," J. Chem. Soc., Faraday Trans. I 73, 968 (1977)

26,15 $^3CH_2 + HCO \rightarrow CH_3 + CO$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with k ~ 3×10^{-11} $cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3. The overall reaction is highly exothermic (381 kJ mol^{-1}).

(R. F. Hampson, May 1984)

26,16 $^3CH_2 + CH_3 \rightarrow C_2H_4 + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		7×10^{-11}	

Comments and Recommendations

The recommended value is that given in Laufer's review and is based on a re-analysis of results of flash photolysis-gas chromatography experiments reported by Laufer and Bass (1975) and by Pilling and Robertson (1975). Uncertainty is a factor of 2.

(R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. M., "Mechanism and Rate Constant of the Reaction between Methylene and Methyl Radicals," J. Phys. Chem. 79, 1635 (1975)

Pilling, M. J., and Robertson, J. A., "Flash Photolysis of Ketene. Photolysis Mechanism and Rate Constants for Singlet and Triplet Methylene," J. Chem. Soc., Faraday Trans. I 73, 968 (1977)

26,17 $^3CH_2 + C_2H_5 \rightarrow CH_3 + C_2H_4$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with k ~ 3×10^{-11} $cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3. The overall reaction is highly exothermic (305 kJ mol^{-1}).

(R. F. Hampson, May 1984)

26,18 $^3CH_2 + C_2H_4 \rightarrow C_3H_6$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$< 3x10^{-14}$	

Comments and Recommendations

The recommended value is the upper limit given in Laufer's review and is based on results reported by Laufer and Bass (1975) and Rowland et al. (1972).

(R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. M., "Mechanism and Rate Constant of the Reaction between Methylene and Methyl Radicals," J. Phys. Chem. 79, 1635 (1975)

Rowland, F. S., Lee, P. S.-T., Montague, D. C., and Russell, R. L., "Tracer Studies of the Reactions of Singlet and Triplet Methylene in the Gas Phase," Faraday Discuss. Chem. Soc. 53, 111 (1972)

26,19 $^3CH_2 + C_2H_3 \rightarrow CH_3 + C_2H_2$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with $k \sim 3x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

26,20 $^3CH_2 + C_2H_2 \rightarrow C_3H_4$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$5.8x10^{-12}$	
Vinckier, Debruyn (1979)	295		$1.3x10^{-12}$	

Comments and Recommendations

The recommended value is that given in Laufer's review and is based on results of flash photolysis-gas chromatography experiments reported by Laufer and Bass (1974) and by Pilling and Robertson (1977). Uncertainty is a factor of 2.

(R. F. Hampson, May 1984)

References

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

Laufer, A. H., and Bass, A. M., "Rate Constants for Reactions of Methylene with Carbon Monoxide, Oxygen, Nitric Oxide, and Acetylene," J. Phys. Chem. 78, 1344 (1974)

Pilling, M. J., and Robertson J. A., "Flash Photolysis of Ketene. Photolysis Mechanism and Rate Constants for Singlet and Triplet Methylene," J. Chem. Soc., Faraday Trans. I 73, 968 (1977)

Vinckier, C., and Debruyn, W., "Reactions of Methylene in the Oxidation Process of Acetylene with Oxygen Atoms at 295 K," Symp. Combust. 17 (Combustion Institute, Pittsburgh, PA 1979) 623

26,21 $^3CH_2 + C_2H \rightarrow CH + C_2H_2$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with k ~ $3x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

26,22 $^3CH_2 + CH_3CO \rightarrow CH_3 + CH_2CO$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with k ~ $3x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

26,23 $^3CH_2 + CH_3O_2 \rightarrow HCHO + CH_3O$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with k ~ $3x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

26,24 $^3CH_2 + CH_3O \rightarrow CH_3 + HCHO$

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with k ~ $3x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3.

(R. F. Hampson, May 1984)

26,25 $^3CH_2 + {}^1CH_2 \rightarrow C_2H_2 + 2H$ (a)
$\rightarrow C_2H_2 + H_2$ (b)

Comments and Recommendations

There are no direct measurements on this system. One expects a fast addition process with k ~ $3x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the hot adduct. The uncertainty is a factor of 3. Reaction channel (b) is much more exothermic than (a) (577 kJ mol^{-1} vs 138 kJ mol^{-1}) and we expect it will be preferred.

(R. F. Hampson, May 1984)

26,26 $^3CH_2 + {}^3CH_2 \rightarrow$ products

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Laufer (1981) review	298		$5.3x10^{-11}$	

Comments and Recommendations

The recommended value is that given in Laufer's review and is based on results of experiments reported by Braun et al. (1970) using flash photolysis and kinetic spectroscopy. The products are $C_2H_2 + H_2$ and $C_2H_2 + 2H$, but the branching ratio has not been measured directly. Uncertainty is a factor of 2.

(R. F. Hampson, May 1984)

References

Braun, W., Bass, A. M., and Pilling, M., "Flash Photolysis of Ketene and Diazomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene," J. Chem. Phys. 52, 5131 (1970)

Laufer, A. H., "Kinetics of Gas Phase Reactions of Methylene," Rev. Chem. Intermediates 4, 225 (1981)

4. **Thermodynamic Data Tables**

Thermodynamic properties of H_2 (Species No. 2)

	J mol^{-1}K^{-1}		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	28.844	130.754	0.000	0.000
500	29.259	145.628	0.000	0.000
700	29.439	155.498	0.000	0.000
900	29.907	162.950	0.000	0.000
1100	30.543	169.008	0.000	0.000
1300	31.338	174.172	0.000	0.000
1500	32.300	178.724	0.000	0.000

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of O_2 (Species No. 3)

	J mol^{-1}K^{-1}		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	29.384	205.213	0.000	0.000
500	31.091	220.589	0.000	0.000
700	32.982	231.363	0.000	0.000
900	34.359	239.827	0.000	0.000
1100	35.309	246.818	0.000	0.000
1300	35.999	252.776	0.000	0.000
1500	36.551	257.969	0.000	0.000

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of H (Species No. 4)

	J mol^{-1}K^{-1}		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	20.786	114.734	217.999	203.188
500	20.786	125.357	219.242	192.970
700	20.786	132.348	220.463	182.247
900	20.786	137.574	221.656	171.167
1100	20.786	141.746	222.794	159.829
1300	20.786	145.218	223.857	148.285
1500	20.786	148.193	224.836	136.587

$$\log K_p = 3.04786 - 11787.9/T + 110229/T^2 - 9.49409x10^6/T^3$$

May, 1983

Stull, D. R., and Prophet, H., JANAF T hemical Tables, NSRDS-NBS 37, U.S. Governmen ing Office, Washington D.C. 20402, 1971

Thermodynamic properties of O (Species No. 5)

	J mol^{-1}K^{-1}		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	21.903	161.088	249.207	231.664
500	21.259	172.092	250.496	219.597
700	21.041	179.205	251.513	207.049
900	20.945	184.481	252.341	194.230
1100	20.895	188.677	253.036	181.243
1300	20.866	192.163	253.647	168.138
1500	20.845	195.150	254.186	154.942

$$\log K_p = 3.49514 - 13390.7/T + 102605/T^2 - 8.7986x10^6/T^3$$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of OH (Species No. 6)

	$J\ mol^{-1}K^{-1}$		$kJ\ mol^{-1}$	
T/K	C_p	S	ΔH_f	ΔG_f
300	29.978	183.782	39.463	34.719
500	29.518	198.953	39.472	31.547
700	29.665	208.895	39.242	28.414
900	30.263	216.413	38.886	25.363
1100	31.125	222.568	38.518	22.397
1300	32.045	227.840	38.175	19.502
1500	32.916	232.488	37.865	16.652

$\log K_p = 0.7388 - 1976.8/T - 18230.2/T^2$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of HO_2 (Species No. 7)

	$J\ mol^{-1}K^{-1}$		$kJ\ mol^{-1}$	
T/K	C_p	S	ΔH_f	ΔG_f
300	34.924	227.748	10.460	23.313
500	39.660	246.689	8.970	32.334
700	43.535	260.684	7.962	41.865
900	46.388	271.985	7.255	51.656
1100	48.585	281.516	6.770	61.576
1300	50.313	289.775	6.431	71.576
1500	51.672	297.077	6.192	81.613

$\log K_p = -2.63079 - 284.219/T - 43292.4/T^2$

May 1983

Entropies and Heat Capacities from: Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37 U.S. Government Printing Office, Washington D.C., 20402, 1971

Enthalpy at 300 K from: Howard, C. J., J. Amer. Chem. Soc. <u>102</u>, 6937 (1980)

Thermodynamic properties of H_2O_2 (Species No. 8)

	$J\ mol^{-1}K^{-1}$		$kJ\ mol^{-1}$	
T/K	C_p	S	ΔH_f	ΔG_f
300	43.221	233.149	-136.135	-105.282
500	52.551	257.588	-138.344	-84.019
700	57.990	276.223	-139.515	-62.057
900	61.463	291.236	-140.231	-39.827
1100	64.141	303.838	-140.674	-17.460
1300	66.400	314.741	-140.934	4.962
1500	68.325	324.381	-141.076	27.422

$\log K_p = -5.88575 + 7432.18/T - 50327.8/T^2$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of H_2O (Species No. 9)

	$J\ mol^{-1}K^{-1}$		$kJ\ mol^{-1}$	
T/K	C_p	S	ΔH_f	ΔG_f
300	33.585	188.929	-241.848	-228.518
500	35.208	206.413	-243.831	-219.078
700	37.464	218.610	-245.643	-208.844
900	39.945	228.321	-247.207	-198.121
1100	42.476	236.584	-248.492	-187.075
1300	44.865	243.877	-249.509	-175.820
1500	46.999	250.450	-250.304	-164.419

$\log K_p = -3.07933 + 13349.9/T - 237272/T^2 + 2.70819\mathrm{x}10^7/T^3$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of CH_4 (Species No. 10)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	35.710	186.368	-74.931	-50.668
500	46.342	206.911	-80.818	-32.823
700	57.794	224.354	-85.475	-12.744
900	67.601	240.099	-88.730	8.489
1100	75.530	254.467	-90.776	30.321
1300	81.747	267.609	-91.927	52.446
1500	86.559	279.659	-92.483	74.722

log K_p = -5.92153 + 5195.06/T - 305478/T^2 + 2.22432x10^7/T^3

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of C_2H_6 (Species No. 11)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	52.706	229.379	-84.098	-31.765
500	77.931	262.245	-93.303	5.812
700	99.127	291.968	-99.747	46.680
900	115.709	318.963	-103.784	89.090
1100	128.570	343.477	-106.073	132.202
1300	138.407	365.790	-107.123	175.628
1500	145.900	386.162	-107.282	219.175

log K_p = -11.6025 + 6208.35/T - 406650/T^2 + 2.58726x10^7/T^3

May 1983

Gurvich, L. V., and Verta, I. V., Thermodynamic Properties of Individual Substances, Vol. 2 Pt 2, Nauka, Moscow, 1979

Thermodynamic properties of HCHO (Species No. 12)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	35.459	218.878	-115.930	-109.863
500	43.765	238.810	-119.265	-104.885
700	52.321	254.935	-122.064	-98.609
900	59.199	268.948	-124.148	-91.621
1100	64.413	281.357	-125.591	-84.241
1300	68.291	292.449	-126.591	-76.626
1500	71.182	302.436	-127.307	-68.873

log K_p = -2.12062 + 6921.06/T - 227782/T^2 + 1.88123x10^7/T^3

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of CO_2 (Species No. 13)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	37.221	213.915	-393.526	-394.413
500	44.627	234.814	-393.677	-394.965
700	49.564	250.663	-394.003	-395.430
900	52.999	263.559	-394.426	-395.790
1100	55.409	274.445	-394.848	-396.049
1300	57.137	283.847	-395.258	-396.229
1500	58.379	292.114	-395.647	-396.342

log K_p = 5.7984x10^{-4} + 20726.6/T - 58681.1/T^2 + 6.05241x10^6/T^3

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of CO (Species No. 14)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	29.142	197.723	-110.516	-137.331
500	29.794	212.719	-110.022	-155.410
700	31.171	222.953	-110.495	-173.502
900	32.577	230.957	-111.449	-191.393
1100	33.710	237.609	-112.608	-209.041
1300	34.572	243.316	-113.880	-226.463
1500	35.217	248.312	-115.215	-243.680

$$\log K_p = 4.36583 + 6328.78/T - 280856/T^2 + 4.24479\text{x}10^7/T^3$$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of HCO (Species No. 15)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	34.606	224.819	37.238	21.912
500	38.426	243.354	36.229	11.945
700	42.288	256.910	34.815	2.473
900	45.551	267.943	33.313	- 6.573
1100	48.133	277.345	31.890	-15.288
1300	50.158	285.554	30.522	-23.753
1500	51.631	292.838	29.121	-32.003

$$\log K_p = 2.16943 - 1478.55/T - 139809/T^2 + 1.32293\text{x}10^7/T^3$$

May 1983

Entropies from: Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C., 20402

Enthalpy at 300 K from: Benson, S. W., "Thermochemical Kinetics," John Wiley and Sons, New York, 1976

McMillen, D. F., and Golden, D. M., "Hydrocarbon Bond Dissociation Energies" in 'Annual Reviews of Physical Chemistry,' B. S. Rabinovitech, Ed., Annual Reviews, Palo Alto, CA, 413 (1982)

Thermodynamic properties of CH_3 (Species No. 16)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	38.752	194.297	145.662	147.934
500	45.250	215.627	142.959	150.193
700	51.175	231.810	140.453	153.544
900	56.526	245.325	138.377	157.565
1100	61.187	257.132	136.792	161.996
1300	65.049	267.680	135.612	166.686
1500	68.153	277.215	134.721	171.548

$$\log K_p = -1.36355 - 6779.94/T - 228890/T^2 + 1.98986\text{x}10^7/T^3$$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of C_2H_5 (Species No. 17)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	50.739	248.291	118.495	145.532
500	71.864	279.223	111.483	165.586
700	88.910	306.235	106.269	188.217
900	102.115	330.239	102.680	212.125
1100	112.412	351.774	100.483	236.689
1300	120.374	371.230	99.232	261.546
1500	126.503	388.899	98.546	286.596

$$\log K_p = -6.71107 - 4667.5/T - 365544/T^2 + 2.67921\text{x}10^7/T^3$$

May 1983

Frequencies and structure from: O'Neal, H. E., and Benson, S. W., "Thermochemistry of Free Radicals," in 'Free Radicals', Vol. II, J.K. Kochi, Ed. (John Wiley and Sons, New York, 1973) pg. 275

Enthalpy at 300 K from: Tsang, W., "Evidence for Strongly Temperature-Dependent A Factors in Alkane Decomposition and High Heats of Formation for Alkyl Radicals," Int. J. Chem. Kinet. 10, 821 (1978)

Thermodynamic properties of C_2H_4 (Species No. 18)

	$J\ mol^{-1}K^{-1}$		$kJ\ mol^{-1}$	
T/K	C_p	S	ΔH_f	ΔG_f
300	43.062	219.488	52.405	68.454
500	62.480	246.107	46.610	80.831
700	77.714	269.676	42.250	95.345
900	89.203	290.654	39.212	110.935
1100	98.019	309.449	37.279	127.081
1300	104.784	326.398	36.141	143.520
1500	109.976	341.774	35.551	160.105

$\log K_p = -4.40757 - 1596.51/T - 235391/T^2 + 1.14816\times10^7/T^3$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of C_2H_3 (Species No. 19)

	$J\ mol^{-1}K^{-1}$		$kJ\ mol^{-1}$	
T/K	C_p	S	ΔH_f	ΔG_f
300	42.032	226.781	286.186	280.441
500	55.559	251.500	282.504	277.650
700	66.300	271.977	279.236	276.307
900	74.680	289.692	276.546	275.830
1100	81.249	305.340	274.516	275.885
1300	86.349	319.348	272.931	276.257
1500	90.295	331.992	271.575	276.880

$\log K_p = -0.21822 - 13953.4/T - 261352/T^2 + 2.1608\times10^7/T^3$

May 1983

Estimated frequencies and structures from ethylene and acetylene: 3300(1), 3000(2), 1800(1), 1400(2), 900(2) 700(1). $I_{xyz} = 2.12 \times 10^{-117}\ g^3cm^6$

Head of formation from: Benson, S. W., "Thermochemical Kinetics," John Wiley and Sons, New York, 1976

Thermodynamic properties of C_2H_2 (Species No. 20)

	$J\ mol^{-1}K^{-1}$		$kJ\ mol^{-1}$	
T/K	C_p	S	ΔH_f	ΔG_f
300	44.229	201.121	226.727	209.058
500	54.869	226.518	226.204	197.405
700	61.149	246.040	225.254	186.046
900	66.111	262.023	224.149	174.979
1100	70.245	275.705	223.145	164.155
1300	73.693	287.729	222.288	153.511
1500	76.530	298.478	221.589	142.997

$\log K_p = 2.75337 - 11526.3/T - 98540.1/T^2 + 9.57154\times10^6/T^3$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Thermodynamic properties of C_2H (Species No. 21)

	$J\ mol^{-1}K^{-1}$		$kJ\ mol^{-1}$	
T/K	C_p	S	ΔH_f	ΔG_f
300	37.175	207.560	534.297	495.093
500	42.819	228.007	534.703	468.775
700	46.614	243.044	534.025	441.743
900	49.647	255.136	532.774	416.496
1100	52.082	265.345	531.343	390.794
1300	54.003	274.211	529.791	365.368
1500	55.497	282.048	528.075	340.188

$\log K_p = 6.42265 - 27220.2/T - 338436/T^2 + 5.05476\times10^7/T^3$

May 1983

Frequencies and structures from: Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

Enthalpy at 300 K based on work of: Okabe, H., and Dibeler, V. H., "Photon Impact Studies of C_2HCN and CH_3CN in the Vacuum UV; Heat of formation of C_2H and CH_3CN," J. Chem. Phys. 59, 2430 (1973)

Thermodynamic properties of CH_3CO (Species No. 22)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	52.208	271.592	-10.209	1.389
500	69.563	302.432	-14.477	10.351
700	83.245	328.118	-17.841	20.907
900	93.504	350.339	-20.309	32.317
1100	101.144	369.878	-21.945	44.187
1300	106.826	387.258	-23.054	56.304
1500	111.073	402.856	-23.907	68.580

$\log K_p = -3.29796 + 1526.99/T - 246148/T^2 + 1.88141x10^7/T^3$

May 1983

Estimated frequencies and moments of inertia from acetaldehyde: 420(1), 760(1), 900(2), 1400(3), 1740(1), 2720(1), 2950(2), 1 free rotor(4.4 x 10^{-40} g cm^2; sym, 3), I_{xyz} = 8.5 x 10^{-116} g^3cm^6

Enthalpy estimated on the basis of the results of:
Watkins, K. W., and Word, W. W., "Addition of Methyl Radicals to Carbon Monoxide: Chemically and Thermally Activated Decomposition of Acetyl Radicals," Int. J. Chem. Kinet. 6, 855 (1974)

Thermodynamic properties of CH_3O (Species No. 24)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	37.949	227.438	16.736	39.853
500	51.852	249.990	11.560	56.777
700	64.321	269.504	7.870	75.563
900	73.885	286.872	5.506	95.240
1100	81.107	302.436	4.197	115.332
1300	86.538	316.448	3.590	135.587
1500	90.630	329.130	3.402	155.921

$\log K_p = -5.45644 + 199.555/T - 256104/T^2 + 1.88549x10^7/T^3$

May 1983

Based on: Burcat, A., and Kudchadker, S., "Ideal Gas Thermodynamic Properties for CH_3O and CH_2OH Radicals," Acta Chim. Acad. Sci. (Hung) 101, 249 (1979)

Thermodynamic properties of CH_3O_2 (Species No. 23)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	54.693	262.914	28.033	71.279
500	74.551	295.750	23.924	101.387
700	88.697	323.227	21.744	132.809
900	98.742	346.791	20.941	164.674
1100	106.110	367.359	21.138	196.610
1300	111.579	385.551	21.966	228.442
1500	115.675	401.819	23.158	260.132

$\log K_p = -8.35953 - 1046.41/T - 11981.8/T^2 - 1.15581x10^7/T^3$

May 1983

Estimated frequencies and moments of inertia: 2930(3), 1400(2), 1350(1), 1100(1), 960(1), 900(2), 450(1), 300(1); I_{xyz} = $72.0g^3$x 10^{-117} g^3cm^6

Enthalpy at 300 K from: Benson, S. W., "Thermochemical Kinetics," John Wiley and Sons, New York, 1976

Thermodynamic properties of $^3CH_2$ (Species No. 26)

	J $mol^{-1}K^{-1}$		kJ mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	34.627	194.033	386.384	360.125
500	37.664	212.430	385.422	357.845
700	40.807	225.593	384.037	347.054
900	44.049	236.241	382.635	336.670
1100	46.978	245.375	381.397	326.586
1300	49.380	253.425	380.321	316.716
1500	51.262	260.626	379.347	307.014

$\log K_p = 2.52768 - 19730.4/T - 136872/T^2 + 1.30419x10^7/T^3$

May 1983

Stull, D. R., and Prophet, H., JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington D.C. 20402, 1971

5. Transport Properties

Parameters in the Lennard-Jones potential used to calculate transport properties pertinent to unimolecular reactions.

Substance	σ (Angstroms)	ϵ/k (K)
Argon	3.542	93.3
Helium	2.551	10.22
Krypton	3.655	178.9
Neon	2.82	32.8
Air	3.711	78.6
Methane	3.758	148.6
Carbon Monoxide	3.690	91.7
Carbon Dioxide	3.941	195.2
Acetylene	4.033	231.8
Ethylene	4.163	224.7
Ethane	4.443	215.7
Hydrogen	2.827	59.7
Nitrogen	3.798	71.4
Oxygen	3.467	106.7
Sulfur Hexafluoride	5.128	222.1
Water	2.641	804.1

$$\log(k(\mathrm{Ar},\ 10)/k\infty) = -0.151 + 5.55\mathrm{x}10^{-4}T - 4.295\mathrm{x}10^{-7}T^2 - 1.081\mathrm{x}10^{-11}T^3$$

In the presence of ethane at 800-900 K, the reverse decomposition rates suggest that step size in deactivation is of the order of 1000 cm^{-1}. On this basis we recommend:

$$\log(k(C_2H_6,\ 0.1)/k\infty) = -0.185 + 9.74\mathrm{x}10^{-4}T - 1.31\mathrm{x}10^{-6}T^2 + 2.05\mathrm{x}10^{-10}T^3$$

$$\log(k(C_2H_6,\ 1)/k\infty) = -0.20 + 8.2\mathrm{x}10^{-4}T - 7.96\mathrm{x}10^{-7}T^2 + 7.45\mathrm{x}10^{-11}T^3$$

$$\log(k(C_2H_6,\ 10)/k\infty) = -0.087 + 2.88\mathrm{x}10^{-4}T - 1.59\mathrm{x}10^{-7}T^2 - 5.64\mathrm{x}10^{-11}T^3$$

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.23	-0.45	-0.71	-0.99	-1.25	-1.52	-1.78	-2.03	-2.28	-2.51	-2.73
16.5	-0.03	-0.12	-0.29	-0.49	-0.72	-0.95	-1.19	-1.42	-1.66	-1.89	-2.10	-2.31
17.0	-0.01	-0.06	-0.17	-0.32	-0.50	-0.69	-0.89	-1.10	-1.31	-1.51	-1.71	-1.90
17.5	0.0	-0.03	-0.09	-0.19	-0.32	-0.47	-0.64	-0.81	-0.99	-1.17	-1.35	-1.53
18.0	0.0	-0.01	-0.04	-0.10	-0.19	-0.30	-0.42	-0.57	-0.72	-0.87	-1.03	-1.18
18.5	0.0	0.0	-0.02	-0.05	-0.10	-0.17	-0.26	-0.37	-0.49	-0.61	-0.74	-0.88
19.0	0.0	0.0	-0.01	-0.02	-0.045	-0.09	-0.15	-0.22	-0.31	-0.40	-0.50	-0.61
19.5	0.0	0.0	0.0	-0.01	-0.02	-0.04	-0.07	-0.12	-0.17	-0.24	-0.31	-0.39
20.0	0.0	0.0	0.0	0.0	-0.01	-0.02	-0.03	-0.06	-0.09	-0.13	-0.17	-0.23
20.5	0.0	0.0	0.0	0.0	0.0	-0.01	-0.01	-0.02	-0.04	-0.06	-0.09	-0.12
21.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.01	-0.015	-0.02	-0.04	-0.05

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.31	0.46	0.56	0.65	0.80
500	0.18	0.30	0.40	0.50	0.69
700	0.11	0.20	0.29	0.39	0.59
900	0.07	0.14	0.21	0.30	0.50
1100	0.046	0.093	0.15	0.23	0.42
1300	0.031	0.069	0.11	0.17	0.35
1500	0.022	0.050	0.082	0.13	0.29
1700	0.015	0.036	0.061	0.10	0.23
1900	0.011	0.026	0.044	0.076	0.19
2100	0.0074	0.018	0.032	0.057	0.15
2300	0.0051	0.013	0.023	0.042	0.12
2500	0.0036	0.009	0.017	0.031	0.09

(W. Tsang, October 1984)

References

Baulch, D. L., and Duxbury, J., "Ethane Decomposition and the Reference Rate Constant for Methyl Radical Recombination," Combust. Flame 37, 313 (1980)

MacPherson, M. T., Pilling, M. J., and Smith, M. J. C., "The Pressure and Temperature Dependence of the Rate Constant for Methyl Radical Recombination over the Temperature Range 296-577 K," Chem. Phys. Lett. 94, 430 (1983)

Quack, M., and Troe, J., "Unimolecular Reactions and Energy Transfer of Highly Excited Molecules," Chapter 5 in Gas Kinetics and Energy Transfer, A Specialist Periodical Report (The Chemical Society, London, 1077) Vol. 2 pg. 175

Roth, P., and Just. Th., "Messungen zur Hochtemperaturpyrolyse von Athan," Ber. Bunsenges. Phys. Chem. 83, 577 (1979)

17,1 $C_2H_5 + M \rightarrow C_2H_4 + M$

Reference	Conditions		Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
	Temp./K	$[M]/molecule\ cm^{-3}$		
Kerr, Lloyd (1968) review			$k_\infty = 2.5x10^{14} exp(-20590/T) s^{-1}$ $k_o = 1x10^{-6} exp(-16000/T)$	

Comments and Recommendations

The data on the forward reaction have been combined with results from lower temperature studies on the reverse reaction to derive the rate expression for decomposition at the high pressure limit. The recommended expression is $k_\infty = 10^{9.69} T^{1.19} exp(-18722/T) s^{-1}$. The k/k_∞ values as a function of pressure and temperature are given in Table A for strong colliders. Collision efficiencies as a function of downward step size and temperature can be found in Table B. On the basis of experiments in the pressure dependent region we find at room temperature downward step sizes of 80 cm^{-1} for H_2, 1000 cm^{-1} for SF_6, 300 cm^{-1} for Kr, 200 cm^{-1} for N_2, 200 cm^{-1} for Ar and, at the higher temperature ranges, 1000 cm^{-1} for ethane. Over the entire temperature range we suggest the use of a 450 cm^{-1} step size down for N_2. This leads to the following fall-off factors:

$$\log(k(N_2,\ 0.1)/k_\infty) = .0678 + 3.365x10^{-4}T - 1.844x10^{-6}T^2 + 3.646x10^{-10}T^3$$
$$\log(k(N_2,\ 1)/k_\infty) = -.236 + 1.349x10^{-3}T - 1993x10^{-6}T^2 + 3.442x10^{-10}T^3$$
$$\log(k(N_2,\ 10)/k_\infty) = -.323 + 1.391x10^{-3}T - 1.457x10^{-6}T^2 + 1.882x10^{-10}T^3$$

For ethyl, a 1000 cm^{-1} step size down leads to the fall-off factors:

$$\log(k(C_2H_5,\ 0.1)/k_\infty) = -.051 + 6.73x10^{-4}T - 1.707x10^{-6}T^2 + 3.083x10^{-10}T^3$$
$$\log(k(C_2H_5,\ 1)/k_\infty) = -.252 + 1.24x10^{-3}T - 1.56x10^{-6}T^2 + 2.325x10^{-10}T^3$$
$$\log(k(C_2H_5,\ 10)/k_\infty) = -.229 + 9.107x10^{-4}T - 8.32x10^{-7}T^2 + 5.016x10^{-11}T^3$$

The overall uncertainty is a factor of 2.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.67	-0.84	-1.11	-1.45	-1.76	-2.07	-2.38	-2.66	-2.93	-3.18	-3.41	-3.62
16.5	-0.35	-0.51	-0.77	-1.06	-1.36	-1.66	-1.95	-2.22	-2.48	-2.72	-2.94	-3.14
17.0	-0.17	-0.29	-0.50	-0.75	-1.02	-1.29	-1.55	-1.81	-2.05	-2.27	-2.48	-2.68
17.5	-0.06	-0.15	-0.30	-0.51	-0.73	-0.96	-1.20	-1.42	-1.64	-1.85	-2.05	-2.23
18.0	-0.02	-0.07	-0.17	-0.31	-0.49	-0.68	-0.88	-1.07	-1.27	-1.45	-1.63	-1.80
18.5	-0.01	-0.03	-0.08	-0.18	-0.30	-0.44	-0.60	-0.76	-0.93	-1.09	-1.24	-1.39
19.0	-0.01	-0.01	-0.04	-0.09	-0.17	-0.27	-0.38	-0.51	-0.64	-0.77	-0.90	-1.02
19.5	0.0	-0.01	-0.01	-0.04	-0.08	-0.14	-0.21	-0.30	-0.40	-0.50	-0.60	-0.70
20.0	0.0	0.0	0.0	-0.01	-0.03	-0.07	-0.11	-0.16	-0.22	-0.30	-0.36	-0.44
20.5	0.0	0.0	0.0	-0.01	-0.01	-0.03	-0.05	-0.08	-0.11	-0.15	-0.19	-0.24
21.0	0.0	0.0	0.0	0.0	0.0	-0.01	-0.02	-0.03	-0.05	-0.07	-0.09	-0.11

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.30	0.50	0.69	0.82
500	0.063	0.16	0.33	0.53	0.71
700	0.031	0.091	0.22	0.40	0.60
900	0.017	0.053	0.14	0.30	0.50
1100	0.0097	0.032	0.09	0.22	0.40
1300	0.0056	0.020	0.06	0.16	0.32
1500	0.0033	0.012	0.038	0.11	0.24
1700	0.0019	0.007	0.024	0.07	0.18
1900	0.0011	0.004	0.015	0.047	0.13
2100	0.00065	0.0025	0.0089	0.030	0.087
2300	0.00036	0.0014	0.0052	0.018	0.057
2500	0.00021	0.0008	0.003	0.011	0.036

(W. Tsang, October 1984)

References

Kerr, J. A., and Lloyd, A. C., "Decomposition Reactions of Radicals," Quart. Rev. 22, 549 (1968)

17,2 $C_2H_5 + H_2 \rightarrow C_2H_6 + H$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
$\log K_p = -1.826 - 834.87/T + 38706/T^2 + 4.954\times10^6/T^3$				
Cao, Back (1982)	1111-1200	1.5×10^{18} H_2 10 ppm C_2H_4	$6.7\times10^{-11}\exp(-11581/T)$	1.5
Baldwin, et al. (1969)	713	$(1-3)\times10^{18}$ H_2 4-15% O_2, 2-3% C_2H_5CHO	2.8×10^{-16}	2
Reid, LeRoy (1968)	513-593	$(1.6-6)\times10^{18}$ H_2 $(2-7)\times10^{16}$ C_2H_4	$3.8\times10^{-12}\exp(-6898/T)$	1.5
Boddy, Steacie (1961)	375-595	$(4-13)\times10^{17}$ 3-pentanone-d_{10} $(4-9)\times10^{-17}$ H_2	$3.4\times10^{-13}\exp(-5690/T)$	1.5

Comments and Recommendations

The experimental results of Baldwin et al. have been rederived using their ratio for $k(C_2H_5 + O_2)/k(C_2H_5 + H_2)$ and the value for $k(C_2H_5 + O_2)$ (17,3) published in 1980. The data of Reid and LeRoy and those of Boddy and Steacie have been recalculated using newer values for the rate of C_2H_5 recombination [17,17]. No corrections have been made for isotope effects. The results are consistent (to within 50%) with the numbers derived from the reverse rate and equilibrium constant. This leads to $k(C_2H_5 + H_2 \rightarrow C_2H_6 + H) = 10^{-23.20}T^{3.6}\exp(-4253/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 1.5 to 700 K, and greater than 4 at 1200 K. The results of Cao and Back are a factor of 4 slower. The activation energy is very high. The results are based on a number of assumptions. Nevertheless their results raise the possibility that our estimated uncertainty may be too optimistic.

(W. Tsang, May 1983)

References

Baldwin, R. R., Walker, R. W., and Langford, D. H., "Reaction of Ethyl Radicals with Hydrogen and Deuterium," Trans. Faraday Soc. 65, 2116 (1969)

Boddy, P. J., and Steacie, E. W. R., "Hydrogen Atom Abstraction by Ethyl-d_5 Radicals. Part II.," Can. J. Chem. 39, 13 (1961)

Cao, J.-R., and Back, M. H., "Kinetics of the reaction $C_2H_5 + H_2 \rightarrow C_2H_6 + H$ from 1111-1200 K," Can. J. Chem. 60, 3039 (1982)

Reid, L. W., and LeRoy, D. J., "The Mercury (6^3P_1) Photosensitized Hydrogenation of Ethylene. Kinetics of the Reaction $C_2H_5 + H_2 = C_2H_6 + H$," Can. J. Chem. 46, 3275 (1968)

17,3 $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ (a)
$\rightarrow C_2H_4O + OH$ (b)
$\rightarrow C_2H_5O_2$ (c)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Baldwin, et al. (1980)	813	$(0.6-6)\times10^{18}$	$k_a = 1.28\times10^{-13}$	1.5
		N_2, O_2, H_2, C_2H_6		
		$(t-C_4H_9)_2$	$k_a = 1.4\times10^{-12}\exp(-1950/T)$	
			$k_b = 1.0\times10^{-13}\exp(-3450/T)$	
Walker (1975) review	753		$k_a = 9\times10^{-14}$	
	896		$k_a = 1.6\times10^{-13}$	
Plumb, Ryan (1981)	295	$(2-34)\times10^{16}$	$k_a = 2.1\times10^{-13}$	2
			$k_c = 4.4\times10^{-12}$	5

Comments and Recommendations

The study of Baldwin et al. involved measuring C_2H_4, C_2H_4O, and butane yields in reacting 2,2,3,3-tetramethylbutane-O_2-ethane systems in boric acid coated vessels. When this was combined with earlier work on propionaldehyde oxidation at lower temperature they obtained the rate expressions given above. Rate constants should be good to ±50%. There is probably considerable uncertainty in the temperature dependence. The activation energy should be small. Note that the recent room temperature value of Plumb and Ryan for k_a is a factor of 100 faster than is predicted by extrapolation of the expression based on higher temperature data. At room temperature the addition reaction is much more important than disproportionation. But due to fall-off effects and the weak $C-O_2$ bond, under combustion conditions disproportionation will be more important. We recommend using the expressions of Baldwin et al. for combustion purposes.

(W. Tsang, May 1983)

References

Baldwin, R. R., Pickering, I. A., and Walker, R. W., "Reactions of Ethyl Radicals with Oxygen over the Temperature Range 400-540 C," J. Chem. Soc., Faraday Trans. I 76, 2374 (1980)

Plumb, I. C., and Ryan, K. R., "Kinetic Studies of the Reaction of C_2H_5 with O_2 at 295 K," Int. J. Chem. Kinet. 13, 1011 (1981)

Walker, R. W., "A Critical Survey of Rate Constants for Reactions in Gas-Phase Hydrocarbon Oxidation," in "Reaction Kinetics," A Specialist Report (The Chemical Society, Burlington House, London, 1975) Vol. 1 pg. 161

17.4 $C_2H_5 + H \rightarrow C_2H_6$ (a)
$\rightarrow CH_3 + CH_3$ (b)
$\rightarrow C_2H_4 + H_2$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Camilleri, et al. (1974)	503-753	$(1-3)x10^{17}$ Ar	$k_b = 6x10^{-11}$ $k_c = 3x10^{-12}$	2
Michael, et al. (1973)	300	$(2.5-15)x10^{16}$ He	$k_{a+b+c} = 3x10^{-11}$	2
Kurylo, et al. (1970)	298	$1.5x10^{18}$ He	$k_{a+b+c} = 6x10^{-11}$	1.5

Comments and Recommendations

Under the experimental conditions of the published work k(b) is the main reaction. We suggest the use of an overall rate of $6.0x10^{-11}cm^3molecule^{-1}s^{-1}$. The branching ratio for k_b/k_a for strong collisions can be found in Table A. Table B contains data on collision efficiencies. k_c is the rate constant for a disproportionation reaction. It should have no activation energy. For reaction in N_2 or polyatomics, on the basis of a step size down of 500 cm^{-1} and 1000 cm^{-1} respectively, we recommend:

$$\log(k_b/k_a(N_2, 0.1)) = -.98 + 2.641x10^{-3}T - 2.0x10^{-7}T^2$$
$$\log(k_b/k_a(N_2, 1)) = -1.915 + 2.69x10^{-3}T - 2.35x10^{-7}T^2$$
$$\log(k_b/k_a(N_2, 10)) = -2.975 + 3.048x10^{-3}T - 3.728x10^{-7}T^2$$

and

$$\log(k_b/k_a(C_2H_6, 0.1)) = -1.168 + 2.4275x10^{-3}T - 1.676x10^{-7}T^2$$
$$\log(k_b/k_a(C_2H_6, 1)) = -2.142 + 2.60x10^{-3}T - 2.44x10^{-7}T^2$$
$$\log(k_b/k_a(C_2H_6, 10)) = -3.263 + 3.061x10^{-3}T - 4.1136x10^{-7}T^2$$

We estimate the uncertainty as a factor of 3.

Table A. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K 300	 500	 700	 900	 1100	 1300	 1500	 1700	 1900	 2100	 2300	 2500
16.0	39	44	63	100	164	268	435	700	1102	1694	2540	3692
16.5	12	14	20.4	32.4	53	87	141	225	353	542	809	1176
17.0	3.9	4.6	6.8	11.0	18	29	47	75	116	177	262	379
17.5	1.3	1.6	2.4	4.0	6.5	10	16.6	26	40	60	88	125
18.0	0.42	0.56	0.91	1.5	2.5	4	6.3	9.7	14.6	21.4	31	43.3
18.5	0.14	0.19	0.35	0.62	1.04	1.7	2.6	3.9	5.7	8.2	11.5	15.1
19.0	0.044	0.066	0.13	0.24	0.43	0.7	1.1	1.7	2.4	3.3	4.6	6.21
19.5	0.013	0.02	0.04	0.09	0.17	0.29	0.47	0.71	1.03	1.4	1.95	2.56
20.0	0.004	0.007	0.015	0.03	0.06	0.11	0.19	0.30	0.44	0.61	0.82	1.07
20.5	0.001	0.002	0.005	0.01	0.02	0.04	0.07	0.11	0.17	0.25	0.34	0.44
21.0				0.003	0.007	0.01	0.02	0.04	0.06	0.09	0.13	0.17

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.52	0.70	0.83
500	0.072	0.18	0.35	0.56	0.73
700	0.040	0.11	0.25	0.44	0.64
900	0.024	0.07	0.18	0.35	0.56
1100	0.015	0.05	0.13	0.28	0.48
1300	0.010	0.033	0.096	0.22	0.41
1500	6.9×10^{-3}	0.024	0.071	0.18	0.35
1700	4.8×10^{-3}	0.017	0.053	0.14	0.30
1900	3.4×10^{-3}	0.012	0.039	0.11	0.25
2100	2.4×10^{-3}	8.6×10^{-3}	0.029	0.085	0.20
2300	1.7×10^{-3}	6.2×10^{-3}	0.021	0.066	0.17
2500	1.2×10^{-3}	4.5×10^{-3}	0.016	0.050	0.13

(W. Tsang, October 1984)

References

Camilleri, P., and Marshall, R. M., and Purnell, J. H., "Reaction of Hydrogen Atoms with Ethane," J. Chem. Soc., Faraday Trans. I 70, 1434 (1974)

Kurylo, M. J., Peterson, N. C., and Braun, W., "Absolute Rates of the Reactions H + C_2H_4 and H + C_2H_5," J. Chem. Phys. 53, 2776 (1970)

Michael, J. V., Osborne, D. T., and Suess, G. N., "Reaction H + C_2H_4: Investigation into the Effects of Pressure, Stoichiometry, and the Nature of the Third Body Species," J. Chem. Phys. 58, 2800 (1973)

17,5 $C_2H_5 + O \rightarrow CH_3CHO + H$ (a)

$\rightarrow HCHO + CH_3$ (b)

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Hoyermann, Sievert (1979)	300	$(0.64\text{-}3.2)\times10^{15}$ He	$k_a/k_b = 5 \pm 1$	

Comments and Recommendations

It is noteworthy that O does not abstract H from ethyl. In view of the well established rate constant of $1.6\times10^{-10} cm^3 molecule^{-1} s^{-1}$ for the analogous CH_3 + O process, a similar value

should hold here. The product distribution suggests 1,2 hydrogen migration to be of considerable importance after addition. The uncertainty is a factor of 2.
(W. Tsang, May 1983)

References

Hoyermann, K., and Sievert, R., "The Reactions of Alkyl Radicals with Oxygen Atoms: Identification of Primary Products at Low Pressure," Symp. Combust. 17, (Combustion Institute, Pittsburgh, 1979) 517

17,6 $C_2H_5 + OH \rightarrow C_2H_4 + H_2O$ (a)
$\rightarrow CH_3 + H + HCHO$ (b)
$\rightarrow C_2H_5OH$ (c)

Comments and Recommendations

In the absence of experimental results it would appear that both abstraction as well as combination must be considered. Chemically activated ethanol can decompose to $C_2H_4 + H_2O$ as in (a) or via C-C bond cleavage to give products as in (b). Unfortunately there have been no determinations on the rate parameters for water elimination from ethanol. Thus the branching ratio for (a+b) and (c) is highly uncertain. At temperatures in excess 800 K and 1 atm N_2 we suggest using: $k_a = k_b = 4x10^{-11}cm^3molecule^{-1}s^{-1}$
The estimated uncertainty is a factor of 4.
(W. Tsang, May 1983)

17,7 $C_2H_5 + HO_2 \rightarrow CH_3 + H_2CO + OH$ (a)
$\rightarrow C_2H_6 + O_2$ (b)
$\rightarrow C_2H_4 + H_2O_2$ (c)

Comments and Recommendations

There are no measurements on this system. We believe that addition will be considerabaly faster than abstraction and this will be followed by rapid decomposition of the adduct. The rate constant, k_a, can be expected to be close to the collisional value $\sim 4x10^{-11}cm^3molecule^{-1}s^{-1}$. Reaction (b) is estimated to have a rate constant of $5x10^{-13}cm^3molecule^{-1}s^{-1}$ and is derived from the estimated rate for the reverse process. Reaction (c) is estimated to have a rate constant of $\sim 5x10^{-13}cm^3molecule^{-1}s^{-1}$ on the basis of disproportionation/combination ratios for normal alkyl radicals. The estimated uncertainties are a factor of 2.
(W. Tsang, May 1983)

17,8 $C_2H_5 + H_2O_2 \rightarrow C_2H_6 + HO_2$

$\log K_p = -1.61927 + 3236.63/T - 64487.6/T^2 + 4.5404\times10^6/T^3$

Comments and Recommendations

In the absence of measurements we have calculated rate parameters on the basis of the rate of the reverse reaction and the equilibrium constant. This yields $k = 1.45\times10^{-14}\exp(-490/T)$ $cm^3molecule^{-1}s^{-1}$. Here as in the methyl radical case, the small rate parameters lead one to suspect that the estimates used in determining the reverse rate expression are in error. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

17,9 $C_2H_5 + H_2O \rightarrow C_2H_6 + OH$

$\log K_p = -3.42 + 0.4 \log T - 4013/T$

Comments and Recommendations

In the absence of experimental data, we recommend the rate expression $k = 5.6\times10^{-18}T^{1.44}\exp(-10150/T)cm^3molecule^{-1}s^{-1}$ on the basis of the recommendation for the rate of the reverse reaction $C_2H_6 + OH \rightarrow C_2H_5 + H_2O$ (see data sheet 11,6) and the equilibrium constant expression derived in Cohen and Westberg (1983). The uncertainty is a factor of 2.

(R. F. Hampson, May 1983)

References

Cohen, N., and Westberg, K., "Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions," J. Phys. Chem. Ref. Data 12, 531 (1983)

17,10 $C_2H_5 + CH_4 \rightarrow C_2H_6 + CH_3$

$\log K_p = -.315613 - 1021.97/T + 5065/T^2 + .21958\times10^7/T^3$

Comments and Recommendations

In the absence of experimental data, on the basis of the well established reverse rate [16,11] and the equilibrium constant we recommend

$k = 1.43\times10^{-25}T^{4.14}\exp(-6322/T)cm^3molecule^{-1}s^{-1}$

The estimated uncertainty is a factor of 2 up to 1000 K.

(W. Tsang, May 1983)

17,12 $C_2H_5 + HCHO \rightarrow C_2H_6 + CHO$

Comments and Recommendations

Rate constants for reactions of alkyl radicals with aldehydic hydrogens are remarkably similar [J. A. Kerr and A. F. Trotman-Dickenson]. We recommend, in the absence of direct measurements, the rate espression for methyl radical attack on formaldehyde:

$$k(C_2H_5 + HCHO \rightarrow C_2H_6 + CHO) = 9.2\mathrm{x}10^{-21}T^{2.81}\exp(-2950/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$$

with an uncertainty of a factor of 2 up to 1000 K and a factor of 5 at 2500 K.

(W. Tsang, May 1983)

References

Kerr, J. A., and Trotman-Dickenson, A. F., "The Reactions of Alkyl Radicals," Progr. React. Kinet. Vol. 1 (Pergamon Press, New York, 1961) pg 105

17,14 $C_2H_5 + CO \rightarrow C_2H_5CO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Watkins, Thompson (1973)	238-378	$(3-75)\mathrm{x}10^{17}$ CO, azoethane	$k\infty = 2.5\mathrm{x}10^{-13}\exp^{-1}/T)/s$	1.3

Comments and Recommendations

The rate constant expression of Watkins and Thompson should be used together with the fall-off corrections for strong colliders given in Table A. Collision efficiencies can be found in Table B. It should be noted that the weak C-CO bond for this system implies that under most conditions the reverse reaction is dominant. We estimate the uncertainty to be a factor of 2. Corrections for weak collisions for N_2 and for larger polyatomics (based on step size down of 500 cm^{-1} and 1000 cm^{-1} respectively) are as follows:

$$\log(k(\mathrm{poly}, 0.1)/k\infty) = 0.299 - 7.589\mathrm{x}10^{-4}T - 1.892\mathrm{x}10^{-6}T^2$$
$$\log(k(\mathrm{poly}, 1)/k\infty) = -0.181 + 1.38\mathrm{x}10^{-3}T - 2.66\mathrm{x}10^{-6}T^2$$
$$\log(k(\mathrm{poly}, 10)/k\infty) = -0.53 + 2.469\mathrm{x}10^{-3}T - 2.705\mathrm{x}10^{-6}T^2$$

$$\log(k(N_2, 0.1)/k\infty) = 0.577 - 2.01\mathrm{x}10^{-3}T - 1.495\mathrm{x}10^{-6}T^2$$
$$\log(k(N_2, 1)/k\infty) = 0.093 + 4.62\mathrm{x}10^{-4}T - 2.52\mathrm{x}10^{-7}T^2$$
$$\log(k(N_2, 10)/k\infty) = 0.423 + 2.296\mathrm{x}10^{-3}T - 3.0299\mathrm{x}10^{-6}T^2$$

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.47	-1.89	-2.33	-2.77	-3.14	-3.45	-3.72	-3.93	-4.10	-4.23	-4.34	-4.43
17.0	-0.67	-1.02	-1.43	-1.83	-2.18	-2.47	-2.73	-2.93	-3.10	-3.23	-3.34	-3.43
18.0	-0.19	-0.41	-0.71	-1.01	-1.30	-1.54	-1.77	-1.96	-2.11	-2.24	-2.35	-2.44
19.0	-0.03	-0.10	-0.24	-0.41	-0.58	-0.74	-0.91	-1.05	-1.18	-1.29	-1.38	-1.46
20.0		-0.02	-0.05	-0.09	-0.15	-0.22	-0.30	-0.37	-0.44	-0.50	-0.56	-0.62
21.0			-0.01	-0.01	-0.02	-0.03	-0.05	-0.07	-0.08	-0.10	-0.12	-0.14

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.11	0.25	0.44	0.64	0.79
500	0.032	0.092	0.22	0.40	0.60
700	0.010	0.034	0.098	0.23	0.42
900	$2.9x10^{-3}$	0.011	0.035	0.098	0.23
1100	$7.6x10^{-4}$	$2.7x10^{-3}$	$9.8x10^{-3}$	0.033	0.093

(W. Tsang, October 1984)

References

Watkins, K. W., and Thompson, W. W., "Addition of Ethyl Radicals to Carbon Monoxide. Kinetic and Thermochemical Properties of the Propionyl Radical", Int. J. Chem. Kinet. 5, 791 (1973)

17,15 C_2H_5 + HCO → C_2H_6 + CO (a)
→ C_2H_5CHO (b)

Comments and Recommendations

There are no measurements. We recommend values similar to those for the corresponding reactions of methyl radicals: k(C_2H_5 + HCO → C_2H_6 + CO) = $2x10^{-10}cm^3molecule^{-1}s^{-1}$ and k(C_2H_5 + HCO → C_2H_5CHO) = $3x10^{-11}cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 3. We have noted earlier that the disproportionation process for the methyl radical seems exceptionally fast.

(W. Tsang, May 1983)

17.16 $C_2H_5 + CH_3 \rightarrow C_3H_8$ (a)
$C_2H_5 + CH_3 \rightarrow CH_4 + C_2H_4$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Gibian, Corley (1972) review	298		$k_b/k_a \sim 0.04$	

Comments and Recommendations

There are no direct measurements. However, one can combine recombination rates for the reaction $2CH_3 \rightarrow C_2H_6$ and $2C_2H_5 \rightarrow C_4H_{10}$ which are well established over extended temperature ranges and through the combination to cross combination ratio determine $k_a^\infty = 4.7\times10^{-11}(300/T)^{0.5\pm0.5}$cm^{3}molecule^{-1}s^{-1}. The pressure dependence for strong colliders is given in Table A. Collision efficiencies as a function of downward step size and temperature can be found in Table B. The high temperature results for the reverse reaction indicate downward step sizes of about 400 cm^{-1} for argon and 600 cm^{-1} for Kr. We suggest the use of step sizes of 450 cm^{-1} for N_2 and 1000 cm^{-1} for larger polyatomics. This leads to the following correction factors at 0.1, 1, 10 atms, and at temperatures in excess of 900 K:

$$\log(k_a(N_2,\ 0.1)/k_a^\infty) = -0.487 + 1.985\times10^{-3}T - 1.874\times10^{-6}T^2 + 2.121\times10^{-10}T^3$$
$$\log(k_a(N_2,\ 1)/k_a^\infty) = -0.3184 + 1.137\times10^{-3}T - 8.353\times10^{-7}T^2 - 2.156\times10^{-11}T^3$$
$$\log(k_a(N_2,\ 10)/k_a^\infty) = -9.683\times10^{-2} + 2.233\times10^{-4}T + 8.8824\times10^{-8}T^2 - 2.0494\times10^{-10}T^3$$

and

$$\log(k_a(C_3H_8,\ 0.1)/k_a^\infty) = -0.357 + 1.347\times10^{-3}T - 1.126\times10^{-6}T^2 + 5.058\times10^{-11}T^3$$
$$\log(k_a(C_3H_8,\ 1)/k_a^\infty) = -0.213 + 6.91\times10^{-4}T - 3.884\times10^{-7}T^2 - 8.8893\times10^{-11}T^3$$
$$\log(k_a(C_3H^8,\ 10)/k_a^\infty) = 2.899\times10^{-2} - 2.382\times10^{-4}T + 4.771\times10^{-7}T^2 - 2.557\times10^{-10}T^3$$

The overall uncertainty is a factor of 2.

The disproportionation channel (b) has been studied by many workers. The rate expression is $k_b = .04\ k_a^\infty$ with an uncertainty of 10%.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K 700	 900	 1100	 1300	 1500	 1700	 1900	 2100	 2300	 2500
16.0	-0.05	-0.17	-0.36	-0.62	-0.91	-1.22	-1.54	-1.85	-2.15	-2.43
16.5	-0.02	-0.09	-0.23	-0.43	-0.67	-0.94	-1.22	-1.50	-1.77	-2.02
17.0	-0.01	-0.05	-0.14	-0.28	-0.47	-0.69	-0.92	-1.17	-1.41	-1.64
17.5		-0.02	-0.07	-0.17	-0.30	-0.47	-0.66	-0.87	-1.08	-1.28
18.0		-0.01	-0.03	-0.09	-0.18	-0.30	-0.45	-0.61	-0.79	-0.95
18.5			-0.01	-0.04	-0.10	-0.18	-0.28	-0.40	-0.54	-0.67
19.0			-0.01	-0.02	-0.04	-0.09	-0.16	-0.24	-0.34	-0.43
19.5				-0.01	-0.02	-0.04	-0.08	-0.13	-0.19	-0.25
20.0					-0.01	-0.02	-0.03	-0.06	-0.09	-0.12
20.5						-0.01	-0.01	-0.02	-0.04	-0.05
21.0								-0.01	-0.01	-0.02

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.3	0.5	0.69	0.82
500	0.065	0.16	0.33	0.54	0.71
700	0.033	0.095	0.22	0.41	0.61
900	0.018	0.057	0.15	0.31	0.51
1100	0.01	0.035	0.09	0.23	0.42
1300	0.006	0.021	0.065	0.16	0.33
1500	0.0036	0.013	0.04	0.11	0.25
1700	0.0021	0.0078	0.026	0.078	0.19
1900	0.0012	0.0046	0.016	0.05	0.13
2100	0.0007	0.0026	0.0094	0.031	0.09
2300	0.00037	0.0012	0.0053	0.018	0.057
2500	0.00019	0.0075	0.0028	0.01	0.034

(W. Tsang, October 1984)

References

Gibian, M. J., and Corley, R. C., "Organic Radical-Radical Reactions Disproportionation vs Combination," Chem. Rev. 73, 443 (1973)

17,17 $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ (a)
$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Parkes, Quinn (1976)	300-850		$k_a = 1.4\times10^{-11}$	1.5
review of pertinent literature together with modulation spectroscopy experiments				
Kerr, Moss (1981)	300-673		$k_b/k_a = 0.13$	
summary of over 30 experiments				
Adachi, et al. (1979)	298	1.5×10^{18} azoethane in propane	$k_a = 2\times10^{-11}$ $k_{a+b} = 2.4\times10^{-11}$	

Comments and Recommendations

We suggest the use of the rate expression $k_a = 1.8\times10^{-11}$ and $k_b = 0.23\times10^{-11}$cm^{3}molecule^{-1}s^{-1} with an uncertainty of 30% over the temperature range 300-1000 K. The instability of C_2H_5 at higher temperature makes the small pressure dependence at high temperature and low pressure unimportant for practical purposes.

(W. Tsang, May 1984)

References

Adachi, H., Basco, N., and James, D. G. L., "A Quantitative Study of Alkyl Radical Reactions by Kinetic Spectroscopy. III. Absorption Spectrum and Rate Constants of Mutual Interaction for the Ethyl Radical," Int. J. Chem. Kinet. 11, 995 (1979)

Kerr, J. A., and Moss, S. J., "CRC Handbook of Bimolecular and Termolecular Reactions," CRC Press, Boca Raton, Florida Vol. II (1981) pg. 80

Parkes, D. A., and Quinn, C. P., "Study of the Spectra and Recombination Kinetics of Alkyl Radicals by Molecular Modulation Spectrometry. Part 2. The Recombination of Ethyl, Isopropyl and t-Butyl Radicals at Room Temperature and t-Butyl Radicals between 250 and 450 K," J. Chem. Soc., Faraday Trans. I 72, 1952 (1976)

18,1 $C_2H_4 \rightarrow C_2H_2 + H_2$ (a)
$\rightarrow C_2H_3 + H$ (b)

Reference	Conditions		Reaction rate constant,	Uncertainty
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Kiefer, et al. (1983)	2300-3200	$(1-3)x10^{18}$ Kr	$k_a = 2.5x10^{-9}exp(-27900/T)$	1.5
			$k_b = 2.3x10^{-9}exp(-41180/T)$	
Tanzawa, Gardiner (1980)	2000-2500	$(1-3)x10^{18}$ Ar	$k_a = 4.9x10^{-7}exp(-40900/T)$	2
			$k_b = 5x10^{-7}exp(-48140/T)$	
Just, et al. (1977)	1700-2200	$(6-16)x10^{18}$	$k_a = 4.3x10^{-7}exp(-39900/T)$	1.5
			$k_b = 6.3x10^{-7}exp(-49400/T)$	

Comments and Recommendations

There is strong evidence that the main reaction in ethylene decomposition involves a molecular channel. Nevertheless, the sequence of reactions initiated by bond breaking will result in the same products. We have extrapolated the experimental data on the basis of RRKM calculations with the molecular process as the sole decomposition channel. Results are given in Table A for strong collisions. Weak collision effects are summarized in Table B. It is interesting to note that over the entire experimental range the reaction is in the intermediate pressure region.
The high pressure rate expression from 1100-2500 K: $k\infty = 10^{12.9}T^{0.44}exp(-44670/T)s^{-1}$ with an uncertainty of a factor of 3.
We have found that the experimental results are consistent with a down step size of 450 cm^{-1} for Argon and Krypton and this is probably also appropriate for N_2.
For large polyatomics we suggest using a step size of 1000 cm^{-1}. On this basis the correction factors to the high pressure rate constants at 0.1, 1, and 10 atm and temperatures in excess of 1000 K for N_2(450 cm^{-1} step size down) and C_2H_4 (1000 cm^{-1} step size down) are as follows:

$$\log(k(N_2,0.1)/k\infty) = 1.044 - 1.174\times10^{-3}T - 1.016\times10^{-7}T^2$$
$$\log(k(N_2, 1)/k\infty) = 0.437 - 2.0917\times10^{-4}T - 2.6622\times10^{-7}T^2$$
$$\log(k(N_2, 10)/k\infty) = -0.162 + 5.156\times10^{-4}T - 3.514\times10^{-7}T^2$$

and

$$\log(k(\mathrm{poly},0.1)/k\infty) = 0.656 - 5.888\times10^{-4}T - 1.871\times10^{-7}T^2$$
$$\log(k(\mathrm{poly}, 1)/k\infty) = 0.073 + 2.19643\times10^{-4}T - 3.035\times10^{-7}T^2$$
$$\log(k(\mathrm{poly}, 10)/k\infty) = -0.32565 + 6.282\times10^{-4}T - 3.09822\times10^{-7}T^2$$

We estimate the uncertainties as a factor of 3.

With respect to the bond breaking reaction, we suggest the use of the experimentally determined expression of Just et al. or Tanzawa and Gardiner in the 1700-2500 K range with argon or N_2 as the third body. At the highest temperatures the expression of Kiefer is more appropriate.

Table A. Values of $\log(k/k\infty)$: dependence on concentration and temperature.

log[M]	T/K 1100	1300	1500	1700	1900	2100	2300
16.0	-0.68	-0.90	-1.11	-1.33	-1.54	-1.75	-1.96
16.5	-0.46	-0.64	-0.83	-1.02	-1.21	-1.40	-1.58
17.0	-0.29	-0.43	-0.59	-0.75	-0.91	-1.08	-1.24
17.5	-0.17	-0.27	-0.39	-0.52	-0.66	-0.80	-0.94
18.0	-0.09	-0.16	-0.24	-0.34	-0.45	-0.56	-0.68
18.5	-0.04	-0.08	-0.13	-0.20	-0.28	-0.37	-0.46
19.0	-0.02	-0.04	-0.07	-0.11	-0.16	-0.22	-0.28
19.5	-0.01	-0.01	-0.03	-0.05	-0.08	-0.12	-0.16
20.0		-0.01	-0.01	-0.02	-0.03	-0.05	-0.08
20.5				-0.01	-0.01	-0.02	-0.03
21.0						-0.01	-0.01

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
1100	0.017	0.053	0.14	0.30	0.50
1300	0.012	0.038	0.11	0.24	0.44
1500	8.4×10^{-3}	0.028	0.082	0.20	0.38
1700	6.1×10^{-3}	0.020	0.063	0.16	0.33
1900	4.5×10^{-3}	0.016	0.050	0.13	0.29
2100	3.4×10^{-3}	0.012	0.039	0.11	0.25
2300	2.5×10^{-3}	9.2×10^{-3}	0.031	0.084	0.21
2500	1.9×10^{-3}	7.1×10^{-3}	0.024	0.072	0.18

(W. Tsang, May 1983)

References

Just, Th., Roth, P., and Damm, R., "Production of Hydrogen Atoms During the Thermal Dissociation of Ethylene between 1700 and 2200 K," Symp. Combust. 16, (Combustion Institute, Pittsburgh, Pa., 1977) 961

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Tanzawa, T., and Gardiner, W. C., Jr., "Thermal Decomposition of Ethylene," Combust Flame 39, 241 (1980)

18,2 $C_2H_4 + H_2 \rightarrow C_2H_5 + H$

$\log K_p = 0.74436 - 14858.89/T - 19924.0/T^2 + 0.58156\times10^7/T^3$

Comments and Recommendations

There are no experimental results on the rate of this reaction. However, on the basis of the rate of the reverse reaction $k(C_2H_5 + H \rightarrow C_2H_4 + H_2) = 3\times10^{-12}\,cm^3 molecule^{-1} s^{-1}$ [Camilleri, P., Marshall, R. M., and Purnell, H., "Reaction of Hydrogen Atoms with Ethane," J. Chem. Soc. Faraday Trans. I 70, 1434 (1974)] and the equilibrium constant we suggest $1.7\times10^{-11}\exp(-34300/T)\,cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 3.
(W. Tsang, May 1983)

18,3 $C_2H_4 + O_2 \rightarrow C_2H_3 + HO_2$

Comments and Recommendations

There are no measurements for the rate of this process. Following Walker's estimates for O_2 + alkane (Reaction Kinetics Vol I, (P. G. Ashmore, Sr. Reporter)), Chemical Society, London, 1974, pg. 161) we assign a rate expression for the abstraction process of $k = 7\times10^{-11}\exp(-29000/T)\,cm^3 molecule^{-1} s^{-1}$, with an uncertainty of a factor of 10. There is, however, the possibility of a lower lying channel involving addition and rearrangement prior to decomposition. Unfortunately we are not able to make any predictions for this process.
(W. Tsang, May 1983)

18,4 $C_2H_4 + H \rightarrow C_2H_5$ (a)

$\rightarrow C_2H_3 + H_2$ (b)

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	$[M]$/molecule cm^{-3}		
(a) Lee, et al. (1978)	198-320	$\sim 1.5 \times 10^{19}$ Ar	$k_a^\infty = 3.67 \times 10^{-11} \exp(-1040/T)$	1.2
Mihelcic, et al. (1975)	300	$\sim 2.5 \times 10^{19}$ Ar	$k_a^\infty = 12.5 \times 10^{-13}$	1.3
Michael, et al. (1973)	300	6×10^{16} to 1.8×10^{19} He also H_2, N_2, Ar, Ne, Kr, SF_6	$k_a^\infty = 16.1 \times 10^{-13}$ also as f(P)	1.5
Kerr, Parsonage (1972) review	300-800		$k_a^\infty = 1.6 \times 10^{-10} \exp(-1410/T)$	
(b) Just, et al. (1977)	2000	$(6\text{-}16) \times 10^{18}$ Ar	$k_b = 2.5 \times 10^{-11}$	1.5
	1700		$k_b = 0.8 \times 10^{-11}$	

Comments and Recommendations

(a) There is good agreement for the value of this rate constant at 300 K. Combining this value with that for the reverse reaction at higher temperatures leads to

$$k(C_2H_4 + H \rightarrow C_2H_5) = 1.42 \times 10^{-15} T^{1.49} \exp(-499/T) cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 1.3.

Throughout most of this range the reaction is in the intermediate pressure region and the pressure dependence, in terms of $\log k/k\infty$ is given in Table A. Collision efficiencies as a function of downward step size and temperature can be found in Table B. The downward step sizes at room temperature are 80 cm^{-1} for H_2, 1000 cm^{-1} for SF_6, 300 cm^{-1} Kr, and 200 cm^{-1} for N_2, Ne and Ar. At higher temperatures the results for the reverse reaction yield a step size of 1000 cm^{-1} for ethane. Over the higher temperature (>600 K) range we suggest the use of a 450 cm^{-1} step size down for N_2. This leads to the following correction factors:

$$\log(k(N_2,\ 0.1)/k\infty) = 0.068 + 3.375 \times 10^{-4} T - 1.844 \times 10^{-6} T^2 + 3.65 \times 10^{-10} T^3$$

$$\log(k(N_2,\ 1)/k\infty) = -0.236 + 1.35 \times 10^{-3} T - 1.99 \times 10^{-6} T^2 + 3.44 \times 10^{-10} T^3$$

$$\log(k(N_2,\ 10)/k\infty) = -0.322 + 1.391 \times 10^{-3} T - 1.457 \times 10^{-6} T^2 + 1.881 \times 10^{-10} T^3$$

For larger polyatomics, a 1000 cm^{-1} step size down leads to the correction factors:

$$\log(k(\text{poly},\ 0.1)/k\infty) = -0.051 + 6.73 \times 10^{-4} T - 1.707 \times 10^{-6} T^2 + 3.083 \times 10^{-10} T^3$$

$$\log(k(\text{poly},\ 10)/k\infty) = 0.252 + 1.24 \times 10^{-3} T - 1.56 \times 10^{-6} T^2 + 2.33 \times 10^{-10} T^3$$

$$\log(k(\text{poly},\ 10)/k\infty) = -0.228 + 9.11 \times 10^{-4} T - 8.32 \times 10^{-7} T^2 + 5.016 \times 10^{-11} T^3$$

The overall uncertainty is a factor of 2.

(b) The work of Just et al. is the only measurement of the rate constant for this reaction channel. We have fit a BEBO calibration to these data yielding $k_b = 2.2 \times 10^{-18} T^{2.53} \exp(-6160/T) cm^3molecule^{-1}s^{-1}$

Table A. Values of log(k/k^{∞}): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.67	-0.84	-1.11	-1.45	-1.76	-2.07	-2.38	-2.66	-2.93	-3.18	-3.41	-3.62
16.5	-0.35	-0.51	-0.77	-1.06	-1.36	-1.66	-1.95	-2.22	-2.48	-2.72	-2.94	-3.14
17.0	-0.17	-0.29	-0.50	-0.75	-1.02	-1.29	-1.55	-1.81	-2.05	-2.27	-2.48	-2.68
17.5	-0.06	-0.15	-0.30	-0.51	-0.73	-0.96	-1.20	-1.42	-1.64	-1.85	-2.05	-2.23
18.0	-0.02	-0.07	-0.17	-0.31	-0.49	-0.68	-0.88	-1.07	-1.27	-1.45	-1.63	-1.80
18.5	-0.01	-0.03	-0.08	-0.18	-0.30	-0.44	-0.60	-0.76	-0.93	-1.09	-1.24	-1.39
19.0	-0.01	-0.01	-0.04	-0.09	-0.17	-0.27	-0.38	-0.51	-0.64	-0.77	-0.90	-1.02
19.5		-0.01	-0.01	-0.04	-0.08	-0.14	-0.21	-0.30	-0.40	-0.50	-0.60	-0.70
20.0				-0.01	-0.03	-0.07	-0.11	-0.16	-0.22	-0.30	-0.36	-0.44
20.5				-0.01	-0.01	-0.03	-0.05	-0.08	-0.11	-0.15	-0.19	-0.24
21.0						-0.01	-0.02	-0.03	-0.05	-0.07	-0.09	-0.11

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.30	0.50	0.69	0.82
500	0.063	0.16	0.33	0.53	0.71
700	0.031	0.091	0.22	0.40	0.60
900	0.017	0.053	0.14	0.30	0.50
1100	0.0097	0.032	0.09	0.22	0.40
1300	0.0056	0.020	0.06	0.16	0.32
1500	0.0033	0.012	0.038	0.11	0.24
1700	0.0019	0.007	0.024	0.07	0.18
1900	0.0011	0.004	0.015	0.047	0.13
2100	0.00065	0.0025	0.0089	0.030	0.087
2300	0.00036	0.0014	0.0052	0.018	0.057
2500	0.00021	0.0008	0.003	0.011	0.036

(W. Tsang, October 1984)

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18,5 $C_2H_4 + O \rightarrow CH_3 + HCO$

Reference	Conditions		Reaction rate constant,	Uncertainty
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Herron, Huie (1973)	200-500		$5.4x10^{-12}exp(-565/T)$	1.2
evaln.	298		$8.1x10^{-13}$	1.2
Peeters, Mahnen (1973)	1200-1700	$3x10^{17}$ O_2, 6.5-7.5% C_2H_4	$3.8x10^{-11}exp(-1360/T)$	
Atkinson, Pitts (1974)	300-392	$2x10^{18}$ Ar	$5.6x10^{-12}exp(-640/T)$	1.2
Singleton, Cvetanovic (1976)	298-486	$2x10^{18}$	$11.6x10^{-12}exp(-845/T)$	1.2
Atkinson, Pitts (1977)	298-439	$7x10^{17}$ Ar	$9.2x10^{-12}exp(-740/T)$	1.2
Nicovich, Ravishankara (1982)	298-940	$2x10^{18}$ Ar	$1.22x10^{-11}exp(-870/T)$ (Arrhenius expression given for 298-438 K)	1.2
Perry (1984)	294-820	$2x10^{18}$ Ar	$2.1x10^{-13}T^{0.63}exp(-690/T)$	1.2

Comments and Recommendations

The recommendation of Herron and Huie (1973) was based on the results reported by Davis et al. (1972) using the flash photolysis-resonance fluorescence technique over the temperature range 230-500 K, with additional room temperature determinations by flash photolysis-kinetic absorption spectroscopy and by discharge flow-mass spectrometry. The present recommendation is derived from a fit to those results, and those of Westenberg and deHaas (1969) for $T<500$ K, Atkinson and Pitts (1974), Singleton and Cvetanovic (1976), Atkinson and Pitts (1977), Nicovich and Ravishankara (1982) and Perry (1984). The recommended rate expresion is $2.2x10^{-16}T^{1.55}exp(-215/T)cm^3molecule^{-1}s^{-1}$ over the range 230-940 K with an uncertainty of 20%.

Until recently, on the basis of final product analysis and also low pressure studies with mass spectrometric detection (Pruss et al. (1974), this reaction was thought to proceed by O atom addition followed by H atom migration in the complex and C-C bond breaking to give predominantly (95%) CH_3 + HCO with a minor channel to give $H_2C_2O + H_2$. However, recent experiments have shown that the vinoxy radical CH_2CHO is a major primary product of this reaction. Buss et al. (1981) in a crossed molecular beam study measured product angular and velocity distribution for all detectable mass peaks. They concluded that the major reaction channel proceeds by H atom elimination to give the vinoxy radical. The addition reaction channel to give CH_3 + HCO was determined to be unimportant in their system. Inoue and Akimoto (1981) have observed by laser induced fluorescence the vinoxy radical produced in this reaction. Kleinermanns and Luntz (1981) also observed this radical by laser induced fluorescence in a crossed molecular beam study of this reaction. Hunziker et al. (1981) studied this reaction in the 40-760 torr pressure range by a photochemical modulation spectroscopy technique. They monitored the transient absorption of CH_2CHO and HCO radicals. Their results indicated that the reaction produced CH_2CHO with 36% yield and CH_3 + HCO with approximately a 55% yield throughout the pressure range studied. The formation of the vinoxy radical as a major primary product has been firmly established but the relative importance of the reaction channels under all conditions has not been determined. (R. F. Hampson, May 1983)

References

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Singleton, D. L., and Cvetanović, R. J., "Temperature Dependence of the Reactions of Oxygen Atoms with Olefins," J. Am. Chem. Soc. 98, 6812 (1976)

Westenberg, A. A., and deHaas, N., "Absolute Measurements of the O + C_2H_4 Rate Coefficient," Symp. Combust. 12, (Combustion Institute, Pittsburgh, 1969) 289

18,6 $C_2H_4 + OH \rightarrow C_2H_3 + H_2O$ (a)
$C_2H_4 + OH(+M) \rightarrow C_2H_4OH(+M)$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
CODATA (1984) evaln.	200-300		$k_b = 9x10^{-12}$ (high pressure limit)	2

Comments and Recommendations

The recommended rate expression for the abstraction reaction is $k_a = 2.6x10^{-20}T^{2.75}exp(-2100/T)$ $cm^3molecule^{-1}s^{-1}$, with an uncertainty of a factor of 10. It is derived from a calculation using the BEBO method as described by Brown (1981). This is the predominant reaction under combustion conditions. At much lower temperatures the reaction proceeds by an addition mechanism for which the recommended expression is that given in the CODATA(1984) evaluation. Under these low temperature conditions the second order rate constant is pressure dependent with appreciable fall-off at pressure below 200 torr He at room temperatures. This dependence upon pressure is largely responsible for the apparent inconsistency among early results reported for various pressures and various diluent gases. In the neighborhood of room temperature the reaction proceeds essentially completely by an addition mechanism with negligible contribution from abstraction pathway.

(R. F. Hampson, May 1983)

References

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CODATA(1984). Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II. CODATA Task Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data 13, 1259 (1984)

18,7 $C_2H_4 + HO_2 \rightarrow C_2H_4O + OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Baldwin, Walker (1981)	773		$8.3x10^{-17}$	
Walker (1974) review	773		$2.4x10^{-17}$	
Lloyd (1974) review	300		$\sim 1.6x10^{-17}$	

Comments and Recommendations

The only measurements from which this rate constant can be estimated are those on the addition of olefins to oxidizing systems. The process is undoubtedly complex. One possibility is $C_2H_4 + HO_2 = C_2H_4OH_2^{\dagger}$ (1,-1), $C_2H_4OH^{\dagger} \rightarrow C_2H_4O + OH$ (2), where the rate constant is given by the expression $k = k_2k_1(k_2 + k_{-1})$. If we use $k_1 \sim 1\text{x}10^{-12}\exp(-4000/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ as appropriate for an addition reaction, then at 773 K, $k_2/k_{-1} \sim 1\text{x}10^{-2}$. We suggest an expression of the form: $k = 1\text{x}10^{-14}\exp(-4000/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. If there is a pressure dependence then $C_2H_4O_2H^{\dagger}$ must be stabilized and this will represent an added complication. Obviously, much more data are needed. The estimated uncertainty is a factor of 3 at 773 K and much larger if long extrapolations are used.

(W. Tsang, May 1983)

References

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18,14 $C_2H_4 + CO \rightarrow C_2H_3 + HCO$

$$\log K_p = 1.9929 - 19901.94/T + 115062/T^2 - 1.90896\text{x}10^7/T^3$$

Comments and Recommendations

There are no measurements on this system. On the basis of an assumed rate constant of $3.3\text{x}10^{-12}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for the reverse reaction we find for the rate of the forward process, $k = 2.5\text{x}10^{-10}\exp(-45600/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$, making it a very unlikely reaction under all combustion conditions. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

18,16 $C_2H_4 + CH_3 \rightarrow C_2H_3 + CH_4$ (a)
$\rightarrow nC_3H_7$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Kerr, Parsonage (1976) review	365-650		$k_a = 7x10^{-13}exp(-5590/T)$	
Kerr, Parsonage (1972) review	400-500		$k_b = 5.5x10^{-13}exp(-3877/T)$	1.3

Comments and Recommendations

Data on the second process are much more extensive than on the first. However at higher temperatures the important process will be (a). Our BEBO calculations match the results quite closely. A fit has been made by changing the activation barrier slightly. This leads to $k(CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3) = 1.1x10^{-23}T^{3.7}exp(-4780/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2.
(W. Tsang, May 1984)

References

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Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals," (Butterworths, London, 1976)

18,17 $C_2H_4 + C_2H_5 \rightarrow C_2H_6 + C_2H_3$ (a)
$\rightarrow 1\text{-}C_4H_9$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
(a) Halstead, Quinn (1968)	798-924	$(1.1-17)x10^{17}$ C_2H_4	$k_a = 6x10^{-13}exp(-8358/T)$	3
(b) Kerr, Parsonage (1972) review			$k_b = 2.5x10^{-13}exp(-3675/T)$	1.2

Comments and Recommendations

(a) The study by Halstead and Quinn is the only published report on the rate for this process. It is derived from studies on the pyrolysis of ethylene and depends on the interpretation of the mechanism. We have revised the expression from that published in order to reflect better established values for k(1-$C_4H_8 \rightarrow C_3H_5 + CH_3$) and k($2C_2H_5 \rightarrow C_4H_{10}$). A fit of the data has been made on the basis of BEBO calculations through a small variation in the activation barrier. This leads to $k_a = 1.05\text{x}10^{-21}T^{3.13}\exp(-9063/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. The estimated uncertainty is a factor of 10.

(b) It should be noted that in most combustion processes the reverse reaction will predominate over the radical combination.
(W. Tsang, May 1983)

References

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18,18 $C_2H_4 + C_2H_4 \rightarrow C_2H_3 + C_2H_5$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
$\log K_p = 1.88585 - 15427.88/T - 156114/T^2 + 2.5437\text{x}10^7/T^3$				
Boyd, et al. (1968)			$1\text{x}10^{-9}\exp(-32200/T)$ (estimate based on reverse process)	
Ayranci, Back (1981)	700-773	$(1\text{-}6)\text{x}10^{18}$ C_2H_4	$2.4\text{x}10^{-8}\exp(-33800/T)$	

Comments and Recommendations

Using the rate of the reverse process (19,17) and the equilibrium constant, we find k($C_2H_4 + C_2H_4 \rightarrow C_2H_3 + C_2H_5$) = $8\text{x}10^{-10}\exp(-36000/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ with an uncertainty of a factor of 10. This expression is at wide variance with the observations of Ayranci and Back.
(W. Tsang, May 1984)

References

Ayranci, G., and Back, M. H., "Kinetics of the Bimolecular Initiation Process in the Thermal Reactions of Ethylene," Int. J. Chem. Kinet. 13, 897 (1981)

Boyd, M. L., Wu, T-M., and Back, M. H., "Kinetics of the Thermal Reactions of Ethylene. Part I," Can. J. Chem. 46, 2415 (1968)

19,1 $C_2H_3 + M \rightarrow C_2H_2 + H + M$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3 molecule^{-1} s^{-1}$	factor
$\log K_p = 5.777 - 8952.6/T + 94313.5/T^2$				
Benson, Haugen (1967)	1300-1800	2.8×10^{19}	$1.3 \times 10^{-9} \exp(-15860/T)$	10
[Skinner, Sokoloski (1960)]	1100-1800	2.8×10^{19} Ar 0.5-6% ethylene		

Comments and Recommendations

There are no direct measurements for this reaction. The work of Benson and Haugen is based on an analysis of the work of Skinner and Sokoloski. The determination of the rates of the reverse reaction is in the temperature range of 193 to 400 K. We have fit the results on the basis of RRKM calculations using these results as a basis. We find, on a strong collision basis, $k_o = 10^{7.88}(1/T)^{3.97}\exp(-21712/T) cm^3 molecule^{-1} s^{-1}$. The corrections for pressure effects can be found in Table A. Collision efficiency as a function of temperature and step size can be found in Table B. The parameters from Benson and Haugen suggest a down step size for argon of ~150 cm^{-1}. We believe a more appropriate step size down for N_2 is 450 cm^{-1} and 1000 cm^{-1} for polyatomics. This leads to the following rate expressions for T>600 K:

$$k(N_2, 0) = 10^{17.84} T^{-7.49} \exp(-22917/T) cm^3 molecule^{-1} s^{-1}$$
$$\log(k(N_2, 0.1)/k(N_2, 0)) = -1.689 + 2.889 \times 10^{-3} T - 1.642 \times 10^{-6} T^2 + 3.045 \times 10^{-10} T^3$$
$$\log(k(N_2, 1)/k(N_2, 0)) = -3.00 + 4.676 \times 10^{-3} T - 2.511 \times 10^{-6} T^2 + 4.497 \times 10^{-10} T^3$$
$$\log(k(N_2, 10)/k(N_2, 0)) = -4.347 + 5.991 \times 10^{-3} T - 2.954 \times 10^{-6} T^2 + 4.994 \times 10^{-10} T^3$$

and with C_2H_3 or similar polyatomics:

$$k(C_2H_3, 0) = 10^{16.67} T^{-6.94} \exp(-22863/T) cm^3 molecule^{-1} s^{-1}$$
$$\log(k(C_2H_3, 0.1)/k(C_2H_3, 0)) = -1.97 + 3.09 \times 10^{-3} T - 1.671 \times 10^{-6} T^2 + 3.01 \times 10^{-10} T^3$$
$$\log(k(C_2H_3, 1)/k(C_2H_3, 0)) = -3.277 + 4.636 \times 10^{-3} T - 2.347 \times 10^{-6} T^2 + 4.056 \times 10^{-10} T^3$$
$$\log(k(C_2H_3, 10)/k(C_2H_3, 0)) = -4.542 + 5.544 \times 10^{-3} T - 2.505 \times 10^{-6} T^2 + 3.99 \times 10^{-10} T^3$$

The rate constants are very much dependent on the uncertain thermochemistry for the vinyl radical. We estimate an uncertainty of a factor of 10 below 1000 K decreasing to a factor of 3 at 2500 K.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.14	-0.10	-0.08	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.02	-0.02	-0.02
16.5	-0.28	-0.19	-0.16	-0.12	-0.10	-0.09	-0.08	-0.06	-0.06	-0.04	-0.04	-0.03
17.0	-0.48	-0.34	-0.27	-0.22	-0.18	-0.16	-0.14	-0.11	-0.10	-0.07	-0.07	-0.06
17.5	-0.76	-0.55	-0.44	-0.36	-0.30	-0.25	-0.22	-0.18	-0.16	-0.12	-0.11	-0.09
18.0	-1.15	-0.83	-0.64	-0.54	-0.45	-0.38	-0.32	-0.27	-0.23	-0.18	-0.16	-0.14
18.5	-1.67	-1.17	-0.94	-0.76	-0.64	-0.53	-0.46	-0.38	-0.33	-0.26	-0.23	-0.20
19.0	-2.13	-1.56	-1.26	-1.04	-0.87	-0.73	-0.63	-0.52	-0.46	-0.37	-0.33	-0.28
19.5	-2.61	-1.99	-1.64	-1.37	-1.14	-0.98	-0.85	-0.71	-0.62	-0.52	-0.46	-0.39
20.0	-3.10	-2.46	-2.07	-1.75	-1.47	-1.28	-1.12	-0.95	-0.83	-0.71	-0.63	-0.55
20.5	-3.60	-2.94	-2.53	-2.18	-1.88	-1.64	-1.42	-1.24	-1.10	-0.95	-0.85	-0.75
21.0	-4.10	-3.43	-3.02	-2.64	-2.30	-2.05	-1.80	-1.59	-1.42	-1.25	-1.12	-1.00

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.69	0.83
500	0.069	0.17	0.35	0.55	0.72
700	0.037	0.10	0.24	0.43	0.63
900	0.022	0.066	0.17	0.34	0.54
1100	0.013	0.043	0.12	0.26	0.46
1300	8.5x10^{-3}	0.028	0.083	0.20	0.38
1500	5.6x10^{-3}	0.019	0.059	0.15	0.32
1700	3.7x10^{-3}	0.013	0.042	0.12	0.26
1900	2.5x10^{-3}	9x10^{-3}	0.03	0.087	0.21
2100	1.7x10^{-3}	6.2x10^{-3}	0.021	0.065	0.17
2300	1.2x10^{-3}	4.3x10^{-3}	0.015	0.048	0.12
2500	7.9x10^{-4}	3.0x10^{-3}	0.011	0.035	0.10

(W. Tsang, October 1984)

References

Benson, S. W., and Haugen, G. R., "Mechanisms for Some High-Temperature Gas-Phase Reactions of Ethylene, Acetylene, and Butadiene," J. Phys. Chem. 71, 1735 (1967)

Skinner, G. B., and Sokoloski, E., "Shock Tube Experiments on the Pyrolysis of Ethylene," J. Phys. Chem. 64, 1028 (1960)

19,2 $C_2H_3 + H_2 \rightarrow C_2H_4 + H$

$\log K_p = -1.14149 + 568.99/T + 136190/T^2 - 2.4092\times10^7/T^3$

Comments and Recommendations

There are no direct measurements for the rate of this process. From the equilibrium constant and the rate of the reverse reaction we derive $k = 5\times10^{-20}T^{2.63}\exp(-4298/T)\,cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 10.

(W. Tsang, May 1983)

19,3 $C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$ (a)
$\rightarrow C_2H_3O_2$ (b)

Comments and Recommendations

There are no measurements on the rates of these processes. By analogy with the reactions of ethyl radicals we estimate $k_a = 2\times10^{-13}cm^3molecule^{-1}s^{-1}$ and $k_b = 1\times10^{-11}cm^3molecule^{-1}s^{-1}$. Under combustion conditions the reverse of (b) predominates, making (a) the more important process. The uncertainty is a factor of 5.

(W. Tsang, May 1983)

19,4 $C_2H_3 + H \rightarrow C_2H_2 + H_2$ (a)
$\rightarrow C_2H_4$ (b)

Comments and Recommendations

There are no experimental results on the rates of these processes. However, in view of the low lying molecular channel for ethylene decomposition (18,1) and on the basis of RRKM calculations it appears that the disproportionation channel (a) will be the most important with a rate constant in the region of $k(C_2H_3 + H \rightarrow C_2H_2 + H_2) = 1.6\times10^{-10}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2.5.

(W. Tsang, May 1983)

19,5 $C_2H_3 + O \rightarrow CH_2CO + H$

Comments and Recommendations

There are no measurements on this process. On the basis of data on the reactions of methyl and ethyl radicals, rates can be expected to be fast $\simeq 1.6\times10^{-10}cm^3molecule^{-1}s^{-1}$. The mechanism involves atom addition followed by adduct decomposition. Uncertainty is a factor of 3.

(W. Tsang, May 1983)

19,6 $C_2H_3 + OH \rightarrow H_2O + C_2H_2$ (a)
$\rightarrow CH_3CHO$ (b)

Comments and Recommendations

There are no measurements on the rate constants for these processes. They should both be close to collisional values ~ $5\times10^{-11}cm^3molecule^{-1}s^{-1}$. Step (a) is an abstraction process, while step (b) involves combination followed by rearrangement. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

19,7 $C_2H_3 + HO_2 \rightarrow OH + CH_2CO + H$

Comments and Recommendations

In the absence of experimental data and since the competing abstraction reaction should be quite slow in comparison to additon, we postulate the reaction to proceed by an addition mechanism with rapid decomposition of the hot adduct. The overall rate constant can be expected to have a near collisional value ~ $5\times10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, May 1983)

19,8 $C_2H_3 + H_2O_2 \rightarrow C_2H_4 + HO_2$

Comments and Recommendations

In the absence of experimental results we estimate this rate constant to be similar to that for the methyl abstraction reaction ~$2\times10^{-14}\exp(300/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 10.

(W. Tsang, May 1983)

19,9 $C_2H_3 + H_2O \rightarrow C_2H_4 + OH$

Comments and Recommendations

There are no reported measurements on this reaction. We suggest the use of a rate expression similar to that for methyl radical attack on water, $k(C_2H_3 + H_2O \rightarrow C_2H_4 + OH) = 8\times10^{-22}T^{2.9}\exp(-7480/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 5 at temperatures above 1000 K and larger at lower temperatures.

(W. Tsang, May 1983)

19,10 $C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3$

$\log K_p = 0.36863 + 381.89/T + 102549/T^2 - 1.2471\times10^7/T^3$

Comments and Recommendations

There are no reported measurements on the rate of this process. We have used the rate expression for the reverse reaction and the equilibrium constant to determine the rate expression $k(C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3) = 2.4\times10^{-24}T^{4.02}\exp(-2754/T)cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 5 at temperatures in excess of 1000 K and larger at lower temperatures.

(W. Tsang, May 1983)

19,11 $C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5$

$\log K_p = 0.68488 + 1403.86/T + 97484/T^2 - 1.46668\times10^7/T^3$

Comments and Recommendations

In the absence of experimental results we have utilized the rate of the reverse reaction [18,17] and the equilibrium constant to yield $k(C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5) = 10^{-21}T^{3.3}\exp(-5285/T)cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 5 at temperatures in excess of 1000 K and larger at lower temperatures.

(W. Tsang, May 1983)

19,12 $C_2H_3 + H_2CO \rightarrow C_2H_4 + HCO$

Comments and Recommendations

In the absence of any direct measurements, we make use of the rate expression for methyl abstraction (16,12) and note the similarities of the rates of abstraction of aldehydic hydrogen by alkyl radicals. (J. A. Kerr and A. F. Trotman-Dickenson, Progr. React. Kinet., Vol. 1, G. Porter and B. Stevens. ed., Pergamon Press, New York, 1961). This leads to the rate expression $9\times10^{-21}T^{2.81}\exp(-2950/T)cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 5 at temperatures in excess of 1000 K and larger at lower temperatures.

(W. Tsang, May 1983)

19,14 $C_2H_3 + CO \rightarrow C_2H_3CO$

Comments and Recommendations

There are no measurements on this reaction. We estimate the enthalpy of reaction to be 117 kJ mol^{-1}. The high pressure rate parameters should be close to that for ethyl + CO or $2.5\times10^{-13}\exp(-2420/T)cm^3molecule^{-1}s^{-1}$. The reaction is in the fall-off region under all conditions. The pressure dependence can be found in Table A. Collision efficiencies as a function of step size and temperature are summarized in Table B. Assuming a step size down of 450 cm^{-1} for N_2 and 1000 cm^{-1} for a polyatomic similar to C_2H_3CO we find the following correction factors at 0.1, 1, and 10 atm respectively:

$$\log(k(N_2,\ 0.1)/k\infty) = -0.129 + 1.07\times10^{-3}T - 2.099\times10^{-6}T^2 + 3.859\times10^{-10}T^3$$

$$\log(k(N_2,\ 1)/k\infty) = -0.34 + 1.5812\times10^{-3}T - 1.848\times10^{-6}T^2 + 2.785\times10^{-10}T^3$$

$$\log(k(N_2,\ 10)/k\infty) = -0.277 + 1.068\times10^{-3}T - 9.225\times10^{-7}T^2 + 4.606\times10^{-11}T^3$$

and

$$\log(k(poly,\ 0.1)/k\infty) = -0.190 + 1.136\times10^{-3}T - 1.784\times10^{-6}T^2 + 2.934\times10^{-10}T^3$$

$$\log(k(poly,\ 1)/k\infty) = -0.282 + 1.208\times10^{-3}T - 1.256\times10^{-6}T^2 + 1.371\times10^{-10}T^3$$

$$\log(k(poly,\ 10)/k\infty) = -0.14 + 4.757\times10^{-4}T - 2.829\times10^{-7}T^2 - 8.537\times10^{-11}T^3$$

The estimated uncertainty is a factor of 5.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.27	-0.5	-0.76	-1.06	-1.36	-1.63	-1.90	-2.15	-2.38	-2.59	-2.79	-2.96
16.5	-0.13	-0.28	-0.5	-0.75	-1.01	-1.26	-1.50	-1.73	-1.94	-2.14	-2.32	-2.50
17.0	-0.05	-0.15	-0.3	-0.50	-0.71	-0.92	-1.13	-1.33	-1.53	-1.71	-1.87	-2.02
17.5	-0.02	-0.07	-0.17	-0.3	-0.46	-0.63	-0.81	-0.98	-1.15	-1.30	-1.45	-1.59
18.0	-0.01	-0.03	-0.08	-0.16	-0.27	-0.39	-0.53	-0.67	-0.81	-0.94	-1.07	-1.19
18.5		-0.01	-0.03	-0.08	-0.14	-0.22	-0.32	-0.42	-0.52	-0.62	-0.72	-0.82
19.0			-0.01	-0.03	-0.06	-0.11	-0.17	-0.23	-0.30	-0.37	-0.44	-0.52
19.5				-0.01	-0.03	-0.05	-0.07	-0.11	-0.15	-0.19	-0.24	-0.29
20.0					-0.01	-0.02	-0.03	-0.04	-0.06	-0.09	-0.11	-0.13
20.5						-0.01	-0.01	-0.02	-0.02	-0.03	-0.04	-0.05
21.0								-0.01	-0.01	-0.01	-0.01	-0.02

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.29	0.49	0.68	0.82
500	0.059	0.15	0.32	0.52	0.70
700	0.029	0.084	0.20	0.38	0.59
900	0.0149	0.047	0.13	0.28	0.48
1100	$7.9x10^{-13}$	0.027	0.079	0.19	0.37
1300	$4.2x10^{-3}$	0.015	0.048	0.13	0.28
1500	$2.3x10^{-3}$	$8.4x10^{-3}$	0.028	0.083	0.20
1700	$1.2x10^{-3}$	$4.6x10^{-3}$	0.016	0.051	0.14
1900	$6.6x10^{-4}$	$2.5x10^{-3}$	$9.1x10^{-3}$	0.030	0.088
2100	$3.4x10^{-4}$	$1.3x10^{-3}$	$4.9x10^{-3}$	0.017	0.17
2300	$1.8x10^{-4}$	$6.9x10^{-4}$	$2.6x10^{-3}$	$9.5X10^{-3}$	0.031
2500	$8.9x10^{-4}$	$3.5x10^{-3}$	$1.35x10^{-3}$	$5.0x10^{-3}$	0.017

(W. Tsang, October 1984)

19,15 $C_2H_3 + HCO \rightarrow C_2H_4 + CO$ (a)
$\rightarrow C_2H_3CHO$ (b)

Comments and Recommendations

There are no rate measurements on these reactions. We suggest values similar to those for methyl + formyl interactions, $k_a = 1.5x10^{-10}cm^3molecule^{-1}s^{-1}$ and $k_b = 3x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3. Due to the small size of acrolein, k_b at higher temperatures will be in the fall off region thus further enhancing k_a. Uncertainty is a factor of 3.

(W. Tsang, May 1983)

19,16 $C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4$ (a)
$\rightarrow C_3H_5 + H$ (b)
$\rightarrow C_3H_6$ (c)

Comments and Recommendations

There are no direct measurements on these processes. We assume that the disproportionation/combination ratio will be similar to that for $CH_3 + C_2H_5$. This leads to $k_a = 6.5\text{x}10^{-13}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ with an uncertainty of a factor of 3. The results for combination and the chemically activated decomposition are summarized in Tables A and B with $k_{b+c}(\infty) = 4.2\text{x}10^{-11}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. Collision efficiency as a function of temperature and step size can be found in Table C.

We suggest using a down step size of 450 cm^{-1} for N_2, O_2, Ar and 1000 cm^{-1} for larger polyatomics. Uncertainties are a factor of 3. As can be seen in Table A, the pressure dependence for k_{b+c} is small. We recommend at 1 atm and with a polyatomic third body the correction factor:

$$\log(k_{b+c}(\text{poly, }1)/k_{b+c}\infty) = -0.177 + 6.687\text{x}10^{-4}T - 6.040\text{x}10^{-7}T^2 + 1.07234\text{x}10^{-10}T^3$$

Within a factor of 1.5, it is also applicable for 0.1 and 10 atm and for N_2 at 0.1, 1, and 10 atm The branching ratio is strongly pressure dependent. The decomposition (b) to stablization (c) ratios for N_2 and polyatomics at 0.1, 1 and 10 atm are:

$\log(k_b/k_c(N_2,\ 0.1)) = 10^{-27.77}T^{8.66}\exp(1639/T)$
$\log(k_b/k_c(N_2,\ 1)) = 10^{-27.95}T^{8.52}\exp(1248/T)$
$\log(k_b/k_c(N_2,\ 10)) = 10^{-30.76}T^{9.16}\exp(1379.3/T)$

and

$\log(k_b/k_c(\text{poly},\ 0.1)) = 10^{-26.25}T^{8.07}\exp(1336.5/T)$
$\log(k_b/k_c(\text{poly},\ 1)) = 10^{-28.07}T^{8.42}\exp(1268/T)$
$\log(k_b/k_c(\text{poly},\ 10)) = 10^{-32.09}T^{9.41}\exp(1650/T)$

Uncertainties are a factor of 5

Table A. Values of $\log(k_{b+c}/k_{b+c}\infty)$: dependence on concentration and temperature.

log[M]	T/K									
	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.17	-0.28	-0.38	-0.47	-0.53	-0.57	-0.60	-0.61	-0.61
16.5	-0.04	-0.11	-0.20	-0.29	-0.39	-0.47	-0.53	-0.57	-0.59	-0.60
17.0	-0.02	-0.06	-0.12	-0.21	-0.30	-0.38	-0.46	-0.51	-0.55	-0.57
17.5	-0.01	-0.03	-0.07	-0.12	-0.20	-0.29	-0.37	-0.43	-0.49	-0.52
18.0		-0.01	-0.03	-0.07	-0.12	-0.19	-0.27	-0.33	-0.39	-0.44
18.5			-0.01	-0.03	-0.07	-0.11	-0.17	-0.23	-0.30	-0.35
19.0				-0.01	-0.03	-0.06	-0.10	-0.14	-0.19	-0.24
19.5					-0.01	-0.03	-0.05	-0.07	-0.10	-0.14
20.0						-0.01	-0.02	-0.03	-0.05	-0.07
20.5							-0.01	-0.02	-0.02	-0.03
21.0								-0.01	-0.01	-0.02

Table B. Values of branching ratio k(decomp)/k(stabl): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	0.006	0.02	0.12	0.28	0.56	1.04	1.89	3.41	6.12	10.91	19.3	33.5
16.5	0.002	0.008	0.052	0.13	0.27	0.50	0.90	1.56	2.73	4.7	8.0	13.3
17.0		0.003	0.02	0.056	0.12	0.24	0.44	0.76	1.28	2.1	3.5	5.7
17.5			0.007	0.023	0.056	0.12	0.21	0.37	0.62	1.0	1.62	2.5
18.0				0.009	0.024	0.05	0.10	0.18	0.31	0.50	0.78	1.18
18.5				0.0017	0.009	0.02	0.048	0.089	0.15	0.25	0.38	0.57
19.0					0.002	0.009	0.021	0.041	0.07	0.12	0.184	0.27
19.5							0.008	0.017	0.03	0.054	0.086	0.13
20.0								0.004	0.013	0.023	0.034	0.056
20.5								0.0014	0.003	0.0087	0.014	0.022
21.0									0.001	0.002	0.003	0.015

Table C. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.14	0.29	0.49	0.68	0.82
500	0.065	0.17	0.33	0.54	0.72
700	0.036	0.10	0.24	0.43	0.62
900	0.022	0.060	0.17	0.34	0.54
1100	0.013	0.043	0.12	0.26	0.46
1300	8.7×10^{-3}	0.029	0.084	0.20	0.39
1500	5.7×10^{-3}	0.020	0.061	0.16	0.32
1700	3.8×10^{-3}	0.013	0.043	0.12	0.26
1900	2.5×10^{-3}	9.2×10^{-3}	0.031	0.088	0.21
2100	1.7×10^{-3}	6.3×10^{-3}	0.022	0.066	0.17
2300	1.1×10^{-3}	4.3×10^{-3}	0.015	0.048	0.13
2500	7.5×10^{-4}	2.9×10^{-3}	0.010	0.034	0.097

(W. Tsang, October 1984)

19,17 $C_2H_3 + C_2H_5 \rightarrow 1\text{-}C_4H_8$ (a)
$\rightarrow C_3H_5 + CH_3$ (b)
$\rightarrow C_2H_4 + C_2H_4$ (c)
$\rightarrow C_2H_2 + C_2H_6$ (d)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Ibuki, Takezaki (1975)	298	$2.3x10^{19}$ H_2	k_c/k_a =0.68 k_d/k_a =0.37	
James, Troughton (1966)	434-448	$9x10_{17}$ 1.1 mixture diethyl ketone diallyl	k_d/k_a =0.12 k_c/k_a =0.034	

Comments and Recommendations

The measurements on the disproportionation to combination ratios are discordant. We favor the lower numbers mainly due to the similarity to that for ethyl disproportionation and combination. Therefore, $k_d = k_c = 0.8x10^{-12}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3. The main reaction is recombination, $k_{a+b} = 2.5x10^{-11}cm^3molecule^{-1}s^{-1}$, where (b) is the decomposition pathway for chemically activated 1-butene with almost no pressure dependence. The branching ratios are given in Table A. Collision efficiencies as a function of step size can be found in Table B. Decomposition to stabilization ratios with nitrogen (450 cm^{-1} step size down) and a polyatomic molecule similar to 1-butene (1000 cm^{-1} step size down) at 0.1, 1 and 10 atm are as follows:

$$\log(k_b/k_a(N_2,\ 0.1)) = 10^{-37.6}T^{12.08}\exp(3946/T)$$
$$\log(k_b/k_a(N_2,\ 1)) = 10^{-35.6}T^{11.25}\exp(3289/T)$$
$$\log(k_b/k_a(N_2,\ 10)) = 10^{-35.03}T^{10.83}\exp(2853/T)$$
$$\log(k_b/k_a(\text{poly},\ 0.1)) = 10^{-19.7}T^{6.7}\exp(25.7/T)$$
$$\log(k_b/k_a(\text{poly},\ 1)) = 10^{-19.0}T^{6.11}\exp(23.70/T)$$
$$\log(k_b/k_a(\text{poly},\ 10)) = 10^{-20.96}T^{6.49}\exp(25.15/T)$$

Uncertainties are a factor of 5.

Table A. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K 300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	0.70	1.14	2.42	5.10	10.3	20.8	41.5	81.4	155	281	476	745.9
16.5	0.23	0.42	0.96	2.04	4.05	7.9	15.3	29.1	53.7	95	158	244
17.0	0.08	0.15	0.38	0.85	1.69	3.26	6.1	11.2	19.8	34	54.7	82.4
17.5	0.024	0.05	0.15	0.35	0.73	1.42	2.61	4.6	7.9	13.9	20.0	29.2
18.0	0.008	0.017	0.05	0.14	0.31	0.63	1.16	2.0	3.32	5.2	7.79	10.9
18.5	0.002	0.006	0.018	0.05	0.12	0.27	0.51	0.90	1.46	2.2	3.2	4.3
19.0		0.002	0.006	0.018	0.05	0.11	0.22	0.39	0.64	0.96	1.35	1.76
19.5			0.002	0.005	0.016	0.04	0.09	0.16	0.27	0.41	0.56	0.72
20.0				0.002	0.005	0.014	0.03	0.06	0.11	0.16	0.22	0.28
20.5					0.002	0.004	0.01	0.02	0.04	0.058	0.08	0.098
21.0						0.001	0.003	0.007	0.01	0.019	0.026	0.033

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
300	0.14	0.30	0.50	0.69	0.82
500	0.064	0.16	0.33	0.53	0.71
700	0.033	0.094	0.22	0.41	0.61
900	0.018	0.056	0.15	0.31	0.51
1100	0.01	0.034	0.097	0.23	0.41
1300	5.9×10^{-3}	0.020	0.062	0.16	0.32
1500	3.5×10^{-3}	0.012	0.040	0.11	0.25
1700	2.0×10^{-3}	7.3×10^{-3}	0.025	0.074	0.18
1900	1.1×10^{-3}	4.2×10^{-3}	0.015	0.048	0.13
2100	6.2×10^{-4}	2.4×10^{-3}	8.6×10^{-3}	0.029	0.084
2300	3.3×10^{-4}	1.3×10^{-3}	4.7×10^{-3}	0.016	0.051
2500	1.6×10^{-4}	6.4×10^{-4}	2.4×10^{-3}	8.8×10^{-3}	0.029

(W. Tsang, October 1984)

References

Ibuki, T., and Takezaki, Y., "The Reaction of Hydrogen Atoms with Acetylene," Bull. Chem. Soc. Jpn. 48, 769 (1975)

James, D. G., and Troughton, G. E., "Reactions of Allylic Radicals," Trans. Faraday Soc. 62, 145 (1966)

19,18 $C_2H_3 + C_2H_4 \rightarrow C_4H_6 + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Benson, Haugen (1967)	1100-1800	2.8x10^{19} Ar 0.5-6% ethylene in argon	8.3x10^{-13}exp(-3676/T)	10

Comments and Recommendations

This expression is based on Benson and Haugen's analysis of the results of Skinner and Sokoloski. The reaction proceeds through the formation of an adduct which rapidly decomposes. The rate parameters are in the range expected for addition reactions and as written the expression is suitable for most high temperature purposes. The uncertainty is a factor of 10.

(W. Tsang, May 1984)

References

Benson, S. W., and Haugen, G. R., "Mechanisms for Some High-Temperature Gas-Phase Reactions of Ethylene, Acetylene, and Butadiene," J. Phys. Chem. 71, 1735 (1967)

Skinner, G. B., and Sokoloski, E. M., "Shock Tube Experiments on the Pyrolysis of Ethylene," J. Phys. Chem. 64, 1028 (1960)

19,19 $C_2H_3 + C_2H_3 \rightarrow C_4H_6$ (a)
$\rightarrow C_2H_2 + C_2H_4$ (b)
$\rightarrow C_4H_5 + H$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
MacFadden, Currie (1973)	298	5x10^{15} divinylether, acetylene, ethylene, CO	k_b - 5x10^{-12}	
Sherwood, Gunning (1965)	323	1x10^{17} divinylmercury	k_b/k_a =0.02	
Weir (1965)	448	1x10^{18} acryaldehyde, vinyl formate	k_b/k_a = 1.0	
Ibuki, Takezaki (1975)	298	2.3x10^{19} He	k_b/k_a = 0.087	

Comments and Recommendations

There is very little definitive information on these reactions. We suggest that recombination of vinyl will be very much like that of ethyl with a high pressure rate of k_{a+c} = 1.6x10^{-11}cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 3. The disproportionation rate is estimated to be 1.6×10^{-12} cm^{3}molecule^{-1}s^{-1}. The results of McFadden and Currie are affected by uncertainties in reaction conditions while those of Sherwood and Gunning and Weir suffer from complexities in the reaction mechanism. The possibility of an exothermic decomposition channel (c) represents an added complication. Results of RRKM calculations on the assumption of strong collisions can be found in Tables A and B. Weak collision effects can be found in Table C. We suggest the use of a down step size of 450 cm^{-1} for N_2 and Argon and 1000 cm^{-1} for large polyatomics. This leads to the following expression:

$$\log(k_{a+c}/k_{a+c\infty}) = -0.040 + 1.044\times10^{-4}T - 5.419\times10^{-9}T^2 - 5.068\times10^{-11}T^3$$

At 1 atm for butadiene this is within a factor of 1.6 of all other results in N_2 and C_4H_6.

Branching ratios are:

$\log(k_c/k_a(N_2, 0.1)) = 10^{-24.6}T^{7.56}\exp(1310/T)$

$\log(k_c/k_a(N_2, 1)) = 10^{-26.9}T^{8.07}\exp(1315/T)$

$\log(k_c/k_a(N_2, 10)) = 10^{-31.3}T^{9.1}\exp(1767/T)$

$\log(k_c/k_a(C_4H_6, 0.1)) = 10^{-24.3}T^{7.36}\exp(1247.7/T)$

$\log(k_c/k_a(C_4H_6, 1)) = 10^{-28.2}T^{8.33}\exp(1565.8/T)$

$\log(k_c/k_a(C_4H_6, 10)) = 10^{-33.3}T^{9.63}\exp(2176.5/T)$

Uncertainty in the rate of vinyl disappearance (k_a+k_c) is a factor of 3, while that for the branching ratio is a factor of 10.

Table A. Values of $\log(k_{a+c}/k_{a+c\infty})$: dependence on concentration and temperature.

log[M]	T/K									
	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.01	-0.02	-0.07	-0.13	-0.22	-0.31	-0.41	-0.51	-0.58	-0.65
16.5		-0.01	-0.04	-0.09	-0.17	-0.25	-0.34	-0.43	-0.52	-0.60
17.0			-0.02	-0.04	-0.10	-0.18	-0.26	-0.35	-0.44	-0.52
17.5			-0.01	-0.02	-0.06	-0.11	-0.18	-0.25	-0.32	-0.42
18.0				-0.01	-0.03	-0.06	-0.11	-0.16	-0.22	-0.30
18.5					-0.01	-0.03	-0.06	-0.10	-0.14	-0.20
19.0						-0.01	-0.03	-0.05	-0.07	-0.11
19.5							-0.01	-0.02	-0.03	-0.05
20.0								-0.01	-0.01	-0.02
20.5										-0.01

Table B. Values of branching ratio k_b/k_a: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	0.013	0.025	0.07	0.15	0.28	0.47	0.76	1.17	1.78	2.7	4.1	6
16.5		0.01	0.026	0.065	0.13	0.23	0.39	0.60	0.90	1.3	1.9	2.7
17.0			0.01	0.026	0.06	0.11	0.20	0.31	0.47	0.68	0.95	1.3
17.5				0.01	0.025	0.05	0.10	0.16	0.24	0.35	0.48	0.64
18.0					0.009	0.02	0.045	0.08	0.12	0.18	0.24	0.32
18.5						0.007	0.019	0.035	0.058	0.086	0.12	0.16
19.0							0.01	0.015	0.025	0.039	0.055	0.07
19.5									0.01	0.016	0.023	0.03
20.0											0.01	0.01

Table C. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.69	0.83
500	0.069	0.17	0.35	0.55	0.72
700	0.037	0.10	0.24	0.43	0.63
900	0.021	0.066	0.17	0.34	0.54
1100	0.014	0.043	0.12	0.26	0.46
1300	8.5×10^{-3}	0.028	0.083	0.20	0.38
1500	5.5×10^{-3}	0.019	0.058	0.15	0.32
1700	3.6×10^{-3}	0.013	0.041	0.11	0.26
1900	2.4×10^{-3}	0.0086	0.029	0.084	0.20
2100	1.6×10^{-3}	0.0057	0.020	0.061	0.16
2300	1.0×10^{-3}	0.0038	0.014	0.043	0.12
2500	6.5×10^{-4}	0.0025	9.0×10^{-3}	0.030	0.087

(W. Tsang, October 1984)

References

Ibuki, T., and Takezaki, Y., "The Reaction of Hydrogen Atoms with Acetylene," Bull. Chem. Soc. Jpn. 48, 769 (1975)

MacFadden, K. O., and Currie, C. L., "Flash Photolysis Studies in a Time-of-Flight Mass Spectrometer. I. Divinyl Ether and Reactions of the Vinyl and Vinoxy Radicals," J. Chem. Phys. 58, 1213 (1973)

Sherwood, A. G., and Gunning, H. E., "The Photolysis of Mercury Divinyl," J. Phys. Chem. 69, 2323 (1965)

Weir, N. A., "Preparation and Reactions of Vinyl Radicals," J. Chem. Soc., 6870 (1965)

20,1 $C_2H_2 \rightarrow C_2H + H$

	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Reference	Temp./K	$[M]$/molecule cm^{-3}		
Tanzawa, Gardiner (1979)	1700-3400	$(6-18)x10^{17}$ 1-10% C_2H_2 in Ar	$7x10^{-8}exp(-53800/T)$	
Frank, Just (1980)	2100-3000	$(3.6-16)x10^{18}$ 5-400 ppm C_2H_2 in Ar	$(6±1)x10^{-8}exp(-53600/T)$	

Comments and Recommendations

The experimental results are in excellent agreement. Both are from shock tube experiments but with different analytical methodology; Frank and Just used resonance absorption with H atom detection and Tanzawa and Gardiner used a variety of methods. At the high temperatures the rates are clearly in the bimolecular region. We have carried out RRKM calculation with a high pressure recombination rate ~$3x10^{-10}cm^3molecule^{-1}s^{-1}$ and confirm Frank and Just's conclusion that for argon in this temperature range the collision efficiency is 0.02. On this basis, one would have expected somewhat greater divergence between the two reported rate expressions. We recommend, on a strong collision basis, $k_o = 10^{9.4}T^{-3.7}exp(-63985/T)cm^3molecule^{-1}s^{-1}$. The departure from a bimolecular process is summarized in Table A. For argon as a third body we find β_c commensurate with a downward step size of 300 cm^{-1}. Since there are no data for other third bodies we suggest using 1000 cm^{-1} for larger polyatomics. Table B give β_c as a function of step size and temperature. The high pressure rate expression is $k\infty = 10^{15.42}exp(-62445/T)s^{-1}$. With N_2 as the weak collider and a step size down of 300 cm^{-1} we find:

$$\log(k(N_2,\ 0.1)/k\infty) = 0.347 - 1.228x10^{-3}T + 3.435x10^{-8}T^2$$
$$\log(k(N_2,\ 1)/k\infty) = 0.178 - 3.966x10^{-4}T - 1.338x10^{-7}T^2$$
$$\log(k(N_2,\ 10)/k\infty) = 0.005 + 7.854x10^{-5}T - 1.775x10^{-7}T^2$$

For C_2H_2 and with a step size down of 1000 cm^{-1} correction factors are:

$$\log(k(C_2H_2,\ 0.1)/k\infty) = 0.476 - 2.015x10^{-3}T + 1.908x10^{-7}T^2$$
$$\log(k(C_2H_2,\ 1)/k\infty) = 0.372 - 1.0081x10^{-3}T - 4.837x10^{-8}T^2$$

and $$\log(k(C_2H_2,\ 10)/k\infty) = 0.129 - 1.951x10^{-4}T - 1.97x10^{-7}T^2$$

The uncertainty is a factor of 3.

Table A. Values of $\log(k/k_o)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.05	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03	-0.03	-0.02	-0.02	-0.02
16.5	-0.16	-0.12	-0.11	-0.10	-0.10	-0.09	-0.07	-0.07	-0.06	-0.06	-0.05	-0.05
17.0	-0.23	-0.27	-0.23	-0.21	-0.20	-0.17	-0.15	-0.14	-0.12	-0.11	-0.11	-0.10
17.5	-0.49	-0.49	-0.43	-0.38	-0.36	-0.31	-0.27	-0.25	-0.23	-0.21	-0.20	-0.18
18.0	-0.85	-0.80	-0.70	-0.62	-0.58	-0.51	-0.45	-0.42	-0.38	-0.35	-0.33	-0.30
18.5	-1.28	-1.20	-1.05	-0.91	-0.87	-0.77	-0.69	-0.66	-0.58	-0.54	-0.51	-0.47
19.0	-1.75	-1.66	-1.46	-1.29	-1.22	-1.10	-1.00	-0.94	-0.85	-0.78	-0.74	-0.68
19.5	-2.24	-2.14	-1.92	-1.72	-1.63	-1.49	-1.37	-1.29	-1.18	-1.09	-1.03	-0.96
20.0	-2.74	-2.63	-2.40	-2.19	-2.08	-1.93	-1.69	-1.69	-1.57	-1.46	-1.38	-1.30
20.5	-3.24	-3.13	-2.89	-2.68	-2.56	-2.40	-2.15	-2.15	-2.00	-1.89	-1.79	-1.60
21.0	-3.74	-3.63	-3.39	-3.18	-3.05	-2.89	-2.63	-2.63	-2.47	-2.34	-2.25	-2.05

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.33	0.53	0.71	0.84
500	0.08	0.20	0.38	0.58	0.75
700	0.049	0.13	0.28	0.48	0.67
900	0.032	0.09	0.22	0.40	0.60
1100	0.022	0.067	0.17	0.34	0.54
1300	0.016	0.05	0.14	0.29	0.49
1500	0.012	0.04	0.11	0.25	0.44
1700	0.0095	0.032	0.091	0.21	0.40
1900	0.0075	0.025	0.076	0.19	0.36
2100	0.006	0.021	0.063	0.16	0.33
2300	0.0049	0.017	0.054	0.14	0.30
2500	0.0041	0.014	0.046	0.12	0.27

(W. Tsang, October 1984)

References

Frank, P., and Just, Th., "High Temperature Thermal Decomposition of Acetylene and Diacetylene at Low Relative Concentrations," Combust. Flame 38, 231 (1980)

Tanzawa, T., and Gardiner, W. C., Jr., "Thermal Decomposition of Acetylene," Symp. Combust. 17, (Combustion Institute, Pittsburgh, Pa., 1979) 563

20,2 $C_2H_2 + H_2 \rightarrow C_2H_4$ (a)
$\rightarrow C_2H_3 + H$ (b)

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log K_p(a) = 7.16094 + 9929.79/T - 136850.9/T^2 + .191006x10^7/T^3

log K_p(b) = 0.07627 - 14215/T - 52582.9/T^2 + 2.54237x10^6/T^3

Comments and Recommendations

There are no direct measurements on these processes. We have calculated the rate constants from the equilibrium constants and the rate constant of reverse processes (-a) (see 18,1) and (-b), assuming a rate constant for the latter of $3\times10^{-12}cm^3molecule^{-1}s^{-1}$ as in C_2H_5 + H. Thus, $k_a = 5\times10^{-13}\exp(-19600/T)cm^3molecule^{-1}s^{-1}$ (see pressure dependence in 18,1) and $k_b = 4\times10^{-12}\exp(-32700/T)cm^3molecule^{-1}s^{-1}$. The uncertainties are a factor of 3 and 10 respectively.

(W. Tsang, May 1984)

20,3 $C_2H_2 + O_2 \rightarrow C_2H + HO_2$

Comments and Recommendations

There are no direct measurements for this process. Following (Walker, R. W., Reaction Kinetics, A Specialist Report (The Chemical Society, Burlington House, London, 1975) Vol. 1, pg. 161), we estimate the rate expression for the abstraction process to be $2\times10^{-11}\exp(-37500/T)cm^3molecule^{-1}s^{-1}$, with an uncertainty of a factor of 10.

There is also the possibility of a low lying decomposition channel involving O_2 addition and rearrangement prior to decomposition. We are not able to make any prediction regarding the likelihood of such a process.

(W. Tsang, May 1983)

20,4 $C_2H_2 + H + M \rightarrow C_2H_3 + M$ (a)
$\rightarrow C_2H + H_2$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
(a) Payne, Stief (1976)	193-400	$2.4\text{-}168\times10^{17}$	$k_a^\infty = 9.2\times10^{-12}\exp(-1213/T)$	1.2
(b) Frank, Just (1980)	1850-3000	$3.6\text{-}16.8\times10^{18}$ Ar	$k_b = 1.3\times10^{-9}\exp(-12900/T)$	5
(a) Sugawara. et al. (1981)	206-461	$5\text{-}6\times10^{19}$ H_2	$k_a^\infty = 3.8\times10^{-11}\exp(-1375/T)$	1.3

Comments and Recommendations

(a) The investigations of Sugawara et al. and Payne and Stief cover extended pressure and temperature ranges. Within a factor of 2 to 3, they are in reasonable accord with other workers (summarized in their papers). We have carried out RRKM calculations in order to reproduce their results and this yields: $k_o = 10^{-16.93}(1/T)^{3.75}\exp(-2430/T)cm^6molecule^{-2}s^{-1}$. Pressure dependence and collision efficiencies as a function of step size down can be found in Tables A and B. The data of Payne and Stief are compatible with a step size of down-100 cm^{-1} for He as a third body. We suggest the use of downward step sizes of 300-400 cm^{-1} for Ar and N_2 and 1000-2000 cm^{-1} for larger polyatomics. On this basis we find for step size down of 450 cm^{-1} and with N_2 as the third body:

$$k(N_2, 0) = 10^{-6.98}T^{-7.27}\exp(-3632/T)cm^6molecule^{-1}s^{-1}$$

$$\log(k(N_2, 0.1)/k(N_2, 0)) = -1.689 + 2.889\times10^{-3}T - 1.642\times10^{-6}T^2 + 3.045\times10^{-10}T^3$$

$$\log(k(N_2, 1)/k(N_2, 0)) = -3.000 + 4.676\times10^{-3}T - 2.511\times10^{-6}T^2 + 4.497\times10^{-10}T^3$$

$$\log(k(N_2, 10)/k(N_2, 0)) = -4.347 + 5.9911\times10^{-3}T - 2.9544\times10^{-6}T^2 + 4.9944\times10^{-10}T^3$$

For C_2H_3 or a similar polyatomic as the bath molecule and with a step size of 1000 cm^{-1}:

$$k(C_2H_3, 0) = 10^{-8.11}T^{-6.73}\exp(-3590/RT)cm^6molecule^{-2}s^{-1}$$

$$\log(k(C_2H_3, 0.1)/k(C_2H_3, 0)) = -1.970 + 3.090\times10^{-3}T - 1.671\times10^{-6}T^2 + 3.012\times10^{-10}T^3$$

$$\log(k(C_2H_3, 1)/k(C_2H_3, 0)) = -3.277 + 4.636\times10^{-3}T - 2.347\times10^{-6}T^2 + 4.056\times10^{-10}T^3$$

$$\log(k(C_2H_3, 10)/k(C_2H_3, 0)) = -4.522 + 5.544\times10^{-3}T - 2.505\times10^{-6}T^2 + 3.990\times10^{-10}T^3$$

The uncertainty is a factor of 4. Note that at temperatures above 1300 K the reaction is near the low pressure limit.

The rate expression given for (b) by Frank and Just is based on a review of past work. We have used the rate expression for the reverse reaction (21,2) derived on the basis of measured numbers at room temperature and a BSBL calculation and the equilibrium constant to derive $k = 10^{-10}\exp(-11200/T)cm^3molecule^{-1}s^{-1}$.

Table A. Values of $\log(k/k_o)$: dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.14	-0.10	-0.08	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.02	-0.02	-0.02
16.5	-0.28	-0.19	-0.16	-0.12	-0.10	-0.09	-0.08	-0.06	-0.06	-0.04	-0.04	-0.03
17.0	-0.48	-0.34	-0.27	-0.22	-0.18	-0.16	-0.14	-0.11	-0.10	-0.07	-0.07	-0.06
17.5	-0.76	-0.55	-0.44	-0.36	-0.30	-0.25	-0.22	-0.18	-0.16	-0.12	-0.11	-0.09
18.0	-1.15	-0.83	-0.64	-0.54	-0.45	-0.38	-0.32	-0.27	-0.23	-0.18	-0.16	-0.14
18.5	-1.67	-1.17	-0.94	-0.76	-0.64	-0.53	-0.46	-0.38	-0.33	-0.26	-0.23	-0.20
19.0	-2.13	-1.56	-1.26	-1.04	-0.87	-0.73	-0.63	-0.52	-0.46	-0.37	-0.33	-0.28
19.5	-2.61	-1.99	-1.64	-1.37	-1.14	-0.98	-0.85	-0.71	-0.62	-0.52	-0.46	-0.39
20.0	-3.10	-2.46	-2.07	-1.75	-1.47	-1.28	-1.12	-0.95	-0.83	-0.71	-0.63	-0.55
20.5	-3.60	-2.94	-2.53	-2.18	-1.88	-1.64	-1.42	-1.24	-1.10	-0.95	-0.85	-0.75
21.0	-4.10	-3.43	-3.02	-2.64	-2.30	-2.05	-1.80	-1.59	-1.42	-1.25	-1.12	-1.00

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.69	0.83
500	0.069	0.17	0.35	0.55	0.72
700	0.037	0.10	0.24	0.43	0.63
900	0.022	0.066	0.17	0.34	0.54
1100	0.013	0.043	0.12	0.26	0.46
1300	8.5×10^{-3}	0.028	0.083	0.20	0.38
1500	5.6×10^{-3}	0.019	0.059	0.15	0.32
1700	3.7×10^{-3}	0.013	0.042	0.12	0.26
1900	2.5×10^{-3}	9×10^{-3}	0.03	0.087	0.21
2100	1.7×10^{-3}	6.2×10^{-3}	0.021	0.065	0.17
2300	1.2×10^{-3}	4.3×10^{-3}	0.015	0.048	0.12
2500	7.9×10^{-4}	3.0×10^{-3}	0.011	0.035	0.10

(W. Tsang, October 1984)

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20,5 $C_2H_2 + O \rightarrow CH_2 + CO$ (a)
$\rightarrow C_2HO + H$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Herron, Huie (1973) evaln.	200-700		$k = 2.3\times10^{-11}\exp(-1500/T)$	1.3
Westenberg, deHaas (1977)	297	$(3-14)\times10^{17}$ Ar	$k = 1.2\times10^{-13}$	1.5
Vandooren, Van Tiggelen (1977)	700-1430	4×10^{17}	$k_a = 1.1\times10^{-10}\exp(-2000/T)$	2.5
Vinckier, Debruyn (1979)	290-600	5×10^{16}	$E_{act} = 3.2\pm0.2$ kcal mol^{-1}	
Aleksandrov, et al. (1981)	298-608	2×10^{16}	$k = 3\times10^{-11}\exp(-1625/T)$	
			$k_b = 1.5\times10^{-11}\exp(-2285/T)$	
Löhr, Roth (1981)	1500-2570	7×10^{17} Ar	$k_a = 2.0\times10^{-10}\exp(-3300/T)$	2
			$k_b = 7.2\times10^{-10}\exp(-6100/T)$	2
NASA (1985) evaln.	200-450		$k = 2.9\times10^{-11}\exp(-1600/T)$	1.5
	298		$k = 1.4\times10^{-13}$	1.3

Comments and Recommendations

This evaluation accepts the NASA (1985) recommendation. Within the stated error limits it should be valid up to 700 K. The results of Aleksandrov et al. are in extremely good agreement. Up to at least 600 K the predominant reaction channel appears to be that giving CH_2 + CO as products with a minor contribution from the channel giving C_2HO + H (see Blumenberg et al. (1977)) and Aleksandrov et al. (1981), although in a molecular beam study both channels were said to be important (Kanofsky et al. (1974). The high temperature results of Lohr and Roth for k_a agree well with those of Vandooren and Van Tiggelen at 1500 K. More high temperature data are needed.

(R. F. Hampson, July 1985)

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Vandooren, J., and Van Tiggelen, P. J., "Reaction Mechanisms of Combustion in Low Pressure Acetylene-Oxygen Flames," Symp. Combust. 16, (Combustion Institute, Pittsburgh, 1977) 1133

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Westenberg, A. A., and deHaas, N., "A Flash Photolysis-Resonance Fluorescence Study of the O + C_2H_2 and O + C_2H_3Cl Reactions," J. Chem. Phys. 66, 4900 (1977)

20,6 $C_2H_2 + OH \rightarrow C_2H + H_2O$ (a)
$\rightarrow$ products (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
CODATA (1984) evaln.	200-300		$6.5\times10^{-12}\exp(-650/T)$ (high pressure limit)	2
	298		7.3×10^{-13}	

Comments and Recommendations

The recommended rate expression for the abstraction reaction is $k_a = 2.4\times10^{-20}T^{2.68}\exp(-6060/T)$ cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 10. It is derived from a calculation using the BEBO method as described by Brown (1981). This is the predominant reaction under combustion conditions. Near room temperature, where there is little agreement on the mechanism, the rate constant, or its pressure dependence, the recommended expression is that given in the CODATA(1984) evaluation. It is based on results reported in Michael et al. (1980). Perry et al. (1977) and Perry and Williamson (1982).

(R. F. Hampson, May 1983)

References

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20,7 $C_2H_2 + HO_2 \rightarrow CH_2{=}C{=}O + OH$ (a)
$\rightarrow CH_2 + CO + OH$ (b)
$\rightarrow HC_2O + H + OH$ (c)

Comments and Recommendations

There are no measurements for the rate constants of these reactions. We suggest as a very rough approximation, with an uncertainty of at least a factor of 10, the same rate expression as for ethylene reacting with HO_2, $k_a = 1\times10^{-14}\exp(-4000/T)cm^3molecule^{-1}s^{-1}$. Reaction paths b and c are also possible. We are unable to estimate branching ratios.
(W. Tsang, May 1983)

20,14 $C_2H_2 + CO \rightarrow C_2H + HCO$

Comments and Recommendations

Since there are no measurements for this reaction we have assumed a reverse rate of $3.3\times10^{-11}cm^3molecule^{-1}s^{-1}$ to obtain $8\times10^{-10}\exp(-53700/T)$ for the forward rate constant with an uncertainty of a factor of 10. This makes it an extremely unlikely process under all combustion conditions.
(W. Tsang, May 1983)

20,16 $C_2H_2 + CH_3 \rightarrow C_3H_5$ (a)
$\rightarrow CH_4 + C_2H$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = -0.8887 - 3718.9/T - 316484/T^2 + 4.332\times10^7/T^3$ (b)				
Holt, Kerr (1977) (a)	379-487	$\sim2\times10^{18}$ i-C_4H_8, ~0.5-8% C_2H_2, ~1% biacetyl	$1\times10^{-12}\exp(-3877/T)$	1.4

Comments and Recommendations

The predominant reaction at low temperature is addition. However at higher temperatures the reaction is reversible. Under combustion conditions the abstraction process is the predominant pathway and, within an uncertainty factor of 5, the rate expression is

$$k(CH_3 + C_2H_2 \rightarrow CH_4 + C_2H) \simeq 3\times10^{-13}\exp(-8700/T)cm^3molecule^{-1}s^{-1}$$

derived on the basis of the reverse rate and equilibrium constant. See data sheet [21,10].
(W. Tsang, May 1983)

References

Holt, P. M., and Kerr, A. J., "Kinetics of Gas Phase Addition Reactions of Methyl Radicals. I. Addition to Ethylene, Acetylene, and Benzene," Int. J. Chem. Kinet. 9, 185 (1977)

20,17 $C_2H_2 + C_2H_5 \rightarrow C_2H + C_2H_6$ (a)
$\rightarrow C_4H_7$ (b)

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log K_p = -1.20495 - 4740.87/T - 311418.9/T^2 + 4.551646x10^7/T^3 (a)

Comments and Recommendations

There are no direct measurements on this reaction. We have used the equilibrium constant and results on the reverse reaction [21,11] to derive k($C_2H_2 + C_2H_5 \rightarrow C_2H + C_2H_6$) = 4.5x$10^{-13}$exp(-11800/T) with an uncertainty of a factor of 5. Note that at lower temperatures the addition reaction (b) is the main process. However, as the temperature is increased the decomposition process will become even more important.

(W. Tsang, May 1984)

20,18 $C_2H_2 + C_2H_4 \rightarrow 2C_2H_3$

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log K_p = 1.21776 - 14783.99/T - 188722.9/T^2 + 2.216286x10^7/T^3

Comments and Recommendations

There are no direct measurements for this reaction. We suggest the rate expression 4x10^{-11}exp(-34400/T)cm^3molecule^{-1}s^{-1} with an uncertainty of a factor of 10. This is based on the equilibrium constant, a disproportionation to combination ratio of 0.1 and a vinyl combination rate similar to that for ethyl radicals. See (19,19) on vinyl combination and disproportionation.

(W. Tsang, May 1983)

20,20 $C_2H_2 + C_2H_2 \rightarrow C_2H_3 + C_2H$ (a)
$\rightarrow C_4H_3 + H$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^3molecule^{-1}s^{-1}	Uncertainty factor
log K_p =0.69769 - 18121/T - 402707.9/T^2 + 5.308452x10^7/T^3 (a)				
Back (1971)			k_a = 8.3x10^{-9}exp(-35250/T)	
Tanzawa, Gardiner (1979)			k_b = 1.6x10^{-11}exp(-23100/T)	

Comments and Recommendations

There are no direct measurements on these processes. Back's results are based on an assumed disproportionation to combination ratio of 1.0 and a combination rate equal to that of ethyl+ethyl (1.6x$10^{-11}$$cm^3$molecule^{-1}s^{-1}) and the thermodynamics of the process. The results of Tanzawa and Gardiner are from complex shock tube experiments. We have recalculated, following Back's

procedure, but using a disproportionation/combination ratio of 0.1 and newer thermodynamic data and derived $k(C_2H_2 + C_2H_2 \rightarrow C_2H_3 + C_2H) = 1.6\times10^{-11}\exp(-42500/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ with an uncertainty of a factor of 5. Reaction (b) is likely to be a composite process.
(W. Tsang, May 1983)

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21,2 $C_2H + H_2 \rightarrow C_2H_2 + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Lange and Wagner (1975)	320	1.3×10^{17} He	1.7×10^{-13}	1.3
Laufer, Bass (1979)	300	1.6×10^{18} He	1.5×10^{-13} (relative to $k(C_2H + C_2H_2)$)	1.3
Okabe (1981)	298		$k/k_{ref}=0.0078$ k_{ref}: $C_2H + C_2H_2$	
Renlund, et al. (1981)	300	2.6×10^{16} He	1.2×10^{-11}	
Brown, Laufer (1981)			$1.9\times10^{-11}\exp(-1450/T)$	calculated

Comments and Recommendations

The expression given by Brown and Laufer (1981) is recommended. They calculated a preexponential factor by the bond energy - bond order (BEBO) method and combined this with the value of k at 300 K reported by Laufer and Bass to give this Arrhenius expression. They also showed that the derived temperature dependence is in good agreement with that calculated by the bond strength - bond length (BSBL) method of Bèrces and Dombi (1980) but is much less than that calculated by the BEBO method. The experimental results of Lange and Wagner (1975) by the discharge flow - mass spectrometric technique are in good agreement with those of Laufer and Bass (1979) who measured the decreased absorption of butadiyne from the reaction $C_2H + C_2H_2 \rightarrow C_4H_2 + H$ upon addition of H_2 in the vacuum ultraviolet flash photolysis of C_2H_2. The recent results of Renlund et al. (1981) by time-resolved CH chemiluminescence are much higher and probably refer to the reaction of excited states of C_2H. Estimated uncertainties are ±30% at room temperatures and increasing to a factor of 3 at 2500 K.
(R. F. Hampson, May 1983)

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Renlund, A. M., Shokoohi, F., Reisler, H., and Wittig, C., "Gas-Phase Reactions of $C_2H(\tilde{X}\Sigma^+)$ with O_2, H_2, and CH_4 Studies Via Time Resolved Product Emissions," Chem. Phys. Lett. 84, 293 (1981)

21,3 $C_2H + O_2 \rightarrow CO + HCO$ (a)
$\rightarrow HC_2O + O$ (b)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Lange, Wagner (1975)	320	$1.3x10^{17}$ He	$k=5.5x10^{-12}$	1.3 see comments
Renlund, et al. (1981)	300	$2.6x10^{16}$ He	$k=2.1x10^{-11}$	
Laufer, Lechleider (1984)	300		$k_a=4.0x10^{-12}$ $k_b=1.0x10^{-12}$	

Comments and Recommendations

The results of Laufer and Lechleider (1984) using flash photolysis-vacuum ultraviolet spectroscopy techniques are recommended. They are consistent with the results of Lange and Wagner (1975) for the overall rate by the discharge flow-mass spectrometer technique. Renlund et al's recent results by time-resolved chemiluminescence are much higher and probably refer to the reaction of excited states of C_2H. There is considerable uncertainty regarding the nature of the products. These may also include $CH + CO_2$ or $C_2O + OH$. We estimate the experimental uncertainties at ±30%. In the absence of measurements on the temperature dependence we assign a factor of 10 uncertainty at 2500 K.
(R. F. Hampson, May 1984)

References

Lange, W., and Wagner, H. Gg., "Massenspektrometrische Untersuchungen über Erzeugung und Reaktionen von C_2H-Radikalen," Ber. Bunsenges. Phys. Chem. 79, 165 (1975)

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Renlund, A. M., Shokoohi, F., Reisler, H., and Wittig, C., "Reaction of C_2H with O_2: Chemiluminescent Products," J. Phys. Chem. 86, 4165 (1982)

21,4 $C_2H + H + M \rightarrow C_2H_2 + M$ (a)
$C_2H + H \rightarrow C_2 + H_2$ (b)

Comments and Recommendations

There are no direct measurements on this process. On the basis of the reverse process and the thermodynamics we have obtained $k_a = 10^{-17.9}(1/T)^{3.1}\exp(-721/T)\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{s}^{-1}$ [third order] with pressure and collisional efficiencies as given in Tables A and B. We recommend use of a 300 cm^{-1} downward step size for argon and N_2 and a 1000-2000 cm^{-1} downward step size for larger polyatomics. On this basis we recommend $k_a\infty = 3\times10^{-10}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$ with the following pressure corrections:

$$\log(k(N_2,\ 0.1)/k\infty)) = 0.347 - 1.228\times10^{-3}T + 3.435\times10^{-8}T^2$$
$$\log(k(N_2,\ 1)/k\infty)) = 0.005 + 7.854\times10^{-5}T - 1.775\times10^{-7}T^2$$
$$\log(k(N_2,\ 10)/k\infty)) = 0.179 - 3.966\times10^{-4}T - 1.338\times10^{-7}T^2$$

For C_2H_2 and with a step size down of 1000 cm^{-1}, the correction factors are:

$$\log(k(C_2H_2,\ 0.1)/k\infty) = 0.476 - 2.015\times10^{-3}T + 1.908\times10^{-7}T^2$$
$$\log(k(C_2H_2,\ 1)/k\infty) = 0.372 - 1.008\times10^{-3}T - 4.837\times10^{-8}T^2$$
$$\log(k(C_2H_2,\ 10)/k\infty) = 0.129 - 1.951\times10^{-4}T - 1.970\times10^{-7}T^2$$

The uncertainty is a factor of 3.

For reaction (b) a BEBO calculation yields $k_b = 6\times10^{-11}\exp(-14223/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$ with an uncertainty of a factor of 10.

Table A. Values of log(k/k∞): dependence on concentration and temperature.

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.07	-0.05	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03	-0.03	-0.02	-0.02	-0.02
16.5	-0.16	-0.12	-0.11	-0.10	-0.10	-0.09	-0.07	-0.07	-0.06	-0.06	-0.05	-0.05
17.0	-0.23	-0.27	-0.23	-0.21	-0.20	-0.17	-0.15	-0.14	-0.12	-0.11	-0.11	-0.10
17.5	-0.49	-0.44	-0.43	-0.38	-0.36	-0.31	-0.27	-0.25	-0.23	-0.21	-0.20	-0.18
18.0	-0.85	-0.80	-0.70	-0.62	-0.58	-0.51	-0.45	-0.42	-0.38	-0.35	-0.33	-0.30
18.5	-1.28	-1.20	-1.05	-0.91	-0.87	-0.77	-0.69	-0.66	-0.58	-0.54	-0.51	-0.47
19.0	-1.75	-1.66	-1.46	-1.29	-1.22	-1.10	-1.00	-0.94	-0.85	-0.78	-0.74	-0.68
19.5	-2.24	-2.14	-1.92	-1.72	-1.63	-1.44	-1.37	-1.29	-1.18	-1.09	-1.03	-0.96
20.0	-2.74	-2.63	-2.40	-2.19	-2.08	-1.93	-1.69	-1.67	-1.57	-1.46	-1.38	-1.30
20.5	-3.24	-3.13	-2.89	-2.68	-2.56	-2.40	-2.15	-2.15	-2.00	-1.89	-1.79	-1.60
21.0	-3.74	-3.63	-3.39	-3.18	-3.05	-2.89	-2.63	-2.63	-2.47	-2.34	-2.25	-2.05

Table B. Collision efficiency β_c as a function of downward step size and temperature.

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.16	0.33	0.53	0.71	0.84
500	0.08	0.20	0.38	0.58	0.75
700	0.049	0.13	0.28	0.48	0.67
900	0.032	0.09	0.22	0.40	0.60
1100	0.022	0.061	0.17	0.34	0.54
1300	0.016	0.05	0.14	0.29	0.49
1500	0.012	0.04	0.11	0.25	0.44
1700	0.0095	0.032	0.091	0.21	0.40
1900	0.0075	0.025	0.076	0.19	0.36
2100	0.006	0.021	0.063	0.16	0.33
2300	0.0049	0.017	0.054	0.14	0.30
2500	0.0041	0.014	0.046	0.12	0.27

(W. Tsang, October 1984)

21,5 $C_2H + O \rightarrow$ products

Comments and Recommendations

There are no measurements on this process. By analogy with the reactions $O + C_2H_5$ and $O + C_2H_3$ one expects a fast reaction with $k \sim 3\times10^{-11} cm^3 molecule^{-1} s^{-1}$ and highly excited products, possibly CH + CO. The uncertainty is a factor of 3.

(R. F. Hampson, May 1983)

21,6 $C_2H + OH \rightarrow C_2H_2 + O$ (a)
$\rightarrow CH_2 + CO$ (b)

Comments and Recommendations

In the absence of experimental results we suggest that the important reaction will be abstraction or addition followed by decomposition proceeding with a near collisional rate constant of $3\times10^{-11} cm^3 molecule^{-1} s^{-1}$ for each process. The uncertainty is a factor of 10.

(R. F. Hampson, May 1983)

21,7 $C_2H + HO_2 \rightarrow C_2H_2 + O_2$
$\rightarrow HC_2O + OH$

Comments and Recommendations

In the absence of experimental results we suggest that the important reactions will be

abstraction and addition followed by decomposition proceeding with near collisional rate constant of $3\text{x}10^{-11}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for each process. The uncertainty is a factor of 10.
(R. F. Hampson, May 1983)

21,10 $C_2H + CH_4 \rightarrow C_2H_2 + CH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
Laufer (1981)	297	$(1\text{-}6)\text{x}10^{18}$ He	$(1.2\pm0.2)\text{x}10^{-12}$	1.3
Okabe (1981)	298		$k/k_{ref} = 0.032$ k_{ref}: $C_2H + C_2H_2$	
Renlund, et al. (1981)	300	$2.6\text{x}10^{16}$ He	$(4.8\pm1.0)\text{x}10^{-12}$	
Brown, Laufer (1981)			$3\text{x}10^{-12}\exp(-250/T)$	calculated

Comments and Recommendations

The expression given by Brown and Laufer (1981) is recommended. They calculated a preexponential factor by the bond energy-bond order (BEBO) method and combined this with the room temperature value of k reported by Laufer (1981) to give this Arrhenius expression. They also showed that the derived temperature dependence is in good agreement with that calculated by the bond strength-bond length (BSBL) method of Bèrces and Dombi (1980) but is much less than that calculated by the BEBO method. Renlund et al.'s higher results probably refer to the reaction of excited states of C_2H. The estimated uncertainty is a factor of 1.3 at room temperature increasing to a factor of 10 at 2500 K.
(R. F. Hampson, May 1984)

References

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21,11 $C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}		
Laufer (1981)	297	$(0.6-23)x10^{18}$ He	$(6.5\pm0.4)x10^{12}$	1.3
Brown, Laufer (1981)			$6x10^{-12}$	calculated

Comments and Recommendations

The expression given by Brown and Laufer (1981) is recommended. They calculated a pre-exponential factor by the bond energy-bond order (BEBO) method and combined this with the room temperature value of k reported by Laufer (1981) to give the temperature-independent expression shown. They also showed that the derived temperature independence is in good agreement with results of calculations by the bond strength-bond length (BSBL) method of Bèrces and Dombi (1980) whereas a strong temperature dependence is calculated by the BEBO method. The uncertainties are a factor of 1.3 at room temperature and a factor of 3 at 2500 K.

(R. F. Hampson, May 1984)

References

Bèrces, T., and Dombi, J., "Evaluation of the Rate Coefficients and Arrhenius Parameters of Hydrogen Atom Transfer Reactions. I. The Method," Int. J. Chem. Kinet. 12, 123 (1980); ibid "II. Application of the Method," Int. J. Chem. Kinet. 12, 183 (1980)

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21,14 $C_2H + CO \rightarrow C_2HCO$

Comments and Recommendations

There are no measurements on this system. Since the thermochemistry is also uncertain we suggest using rate constants that we have estimated for the $C_2H_3 + CO + (M) \rightarrow C_2H_3CO$ reaction, $k = 2.5x10^{-13}exp(-2420/T)cm^3molecule^{-1}s^{-1}$. Note that at higher temperatures the reaction is reversed. The uncertainty is greater than a factor of 10. Because of this the pressure dependence has been neglected.

(W. Tsang, May 1983)

21,15 $C_2H + HCO \rightarrow C_2H_2 + CO$

Comments and Recommendations

In the absence of experimental results we suggest that the important reaction will be disproportionation proceeding with a near collisional rate constant of 1.0×10^{-10} cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 3.

(R. F. Hampson, May 1983)

21,16 $C_2H + CH_3 \rightarrow C_3H_3 + H$

Comments and Recommendations

Although there are no measurements on this process, the exothermicity of the reaction (~ 117 kJ mol^{-1}) suggests that this will be the preferred channel under practically all combustion situations. We estimate the rate constant for the process to be 4×10^{-11}cm^{3}molecule^{-1}s^{-1}. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

21,17 $C_2H + C_2H_5 \rightarrow C_2H_2 + C_2H_4$ (a)
$\rightarrow C_3H_3 + CH_3$ (b)

Comments and Recommendations

These reactions have not been studied. We estimate $k_a \simeq 3\times10^{-12}$cm^{3}molecule^{-1}s^{-1}, typical of a disproportionation process and $k_b \sim 3\times10^{-11}$cm^{3}molecule^{-1}s^{-1}, a typical rate constant for radical combination. The exothermicity of process (b) ~ 170 kJ mol^{-1} should make this the preferred mode of decomposition (rather than stabilization) for all combustion situations. The uncertainty is a factor of 3.

(W. Tsang, May 1983)

21,18 $C_2H + C_2H_4 \rightarrow C_4H_4 + H$

Comments and Recommendations

In the absence of experimental data, by analogy with the reaction 21,20 $C_2H + C_2H_2$, we suggest this reaction proceeds by a fast addition process with k ~ 2×10^{-11} cm^{3}molecule^{-1}s^{-1} to give an excited C_4H_5 adduct which decomposes to give C_4H_4 (vinyl acetylene) + H. The uncertainty is a factor of 3.

(R. F. Hampson, May 1983)