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Tables of Bimolecular Gas Reactions

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Foreword

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The NSRDS is conducted as a decentralized operation of nation-wide scope with central coordination by NBS. It comprises a complex of data centers and other activities, carried on in government agencies, academic institutions, and nongovernmental laboratories. The independent operational status of existing critical data projects is maintained and encouraged. Data centers that are components of the NSRDS produce compilations of critically evaluated data, critical reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data.

For operational purposes, NSRDS compilation activities are organized into seven categories as listed below. The data publications of the NSRDS, which may consist of monographs, loose-leaf sheets, computer tapes, or any other useful product, will be classified as belonging to one or another of these categories. An additional "General" category of NSRDS publications will include reports on detailed classification schemes, lists of compilations considered to be Standard Reference Data, status reports, and similar material. Thus, NSRDS publications will appear in the following eight categories:

Category	*Title*
1	General
2	Nuclear Properties
3	Atomic and Molecular Properties
4	Solid State Properties
5	Thermodynamic and Transport Properties
6	Chemical Kinetics
7	Colloid and Surface Properties
8	Mechanical Properties of Materials

Within the National Bureau of Standards publication program a new series has been established, called the National Standard Reference Data Series. The present report, which is in Category 6 of the above list, is Number 9 of the new series and is designated NSRDS–NBS 9.

A. V. ASTIN, *Director.*

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Tables of Bimolecular Gas Reactions

A. F. Trotman-Dickenson and G. S. Milne

This survey covers the kinetics of bimolecular and termolecular gas reactions that do not involve atoms or molecules in electronically excited states. Bimolecular reactions are here defined as reactions in which two molecules are involved as reactants, that yield two or more molecules as products. Those reactions in which two molecules combine to form one molecule are most usefully considered as the reverse of unimolecular reactions which will be dealt with in another survey. Reactions of oxygen and nitrogen atoms have been omitted as they will also form the subject of another survey.

The literature from 1954 to December 31, 1965 has been exhaustively searched and it is hoped that for this period nothing has been omitted that should have been included.

The survey of earlier work has been based on one of the writers' books on "Gas Kinetics" which covered the literature to 1954. Use of the book for over ten years has revealed few omissions and these have been included in these tables. Data for the period January to August 1966 has been included where possible.

Key Words: Chemical kinetics, gas, bimolecular, reactions, tables, rate constants, activation energies, Arrhenius equation, data.

Preface

This survey covers the kinetics of bimolecular and termolecular gas reactions that do not involve atoms or molecules in electronically excited states. Bimolecular reactions are here defined as reactions in which two molecules are involved as reactants, that yield two or more molecules as products. Those reactions in which two molecules combine to form one molecule are most usefully considered as the reverse of unimolecular reactions which will be dealt with in another survey. Reactions of oxygen and nitrogen atoms have been omitted as they will also form the subject of another survey.

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Originally it was hoped to make this survey a critical study from which reliable data could be distilled. As the work proceeded it became evident that this was not a realistic goal. Only a small fraction of the reactions has been the subject of investigation by several workers. When several studies have been made the results fall into two classes. In the first class are those reactions that have been repeatedly investigated. It is then usually found that the discrepancies are greater than the random errors and that some systematic differences exist. It is not possible to decide which value is most nearly correct. In the second class are those reactions that have been investigated under widely different conditions. In these cases the best result for one purpose may not be the best for another, so that no useful choice can be made. We therefore decided to make the tables as comprehensive as possible so that users can readily discover what information is available.

It is likely that some reactions have been omitted and that other errors have crept in. We shall be grateful if readers will write to tell us of suggested improvements. It is hoped to publish supplements to these tables every two or three years.

Notes on the Tables

All the rate data is in the simple Arrhenius form $k=Ae^{-E/RT}$. "A" factors and rate constants are in cm. mole. sec. units throughout. Activation energies are in kcal/mole and temperatures in degrees centigrade.

Where data has been represented by equations of the type

$$k=BT^{n}e^{-H/RT} \qquad \left(n=1, \frac{1}{2}, \frac{1}{4}\right),$$

B and H have been converted to the simple form by means of the equations

$$A=e^{n}BT^{n} \text{ and } E=H+nRT,$$

where T is the absolute temperature at the mid-point of the experimental range.

Where the rate equation is reported as a more complex function of temperature, it has been quoted as such in the tables.

Most of the data is for simple radical/molecule metathetical reactions of the type

$$R_1 + R_2X = R_1X + R_2$$

where R_1 is an atom or radical attacking a molecule R_2X. X is the atom transfered in the reaction.

For each radical R_1 there is a separate table (see contents). The first column of each table consists of a list of molecules R_2X with which R_1 reacts. Columns three to five contain the Arrhenius values and the experimental temperature ranges. Column six gives an indication of the nature of the experimental method used to obtain the data.

The following abbreviations have been used in describing the radical source:

P	photolysis.
F.P.	flash photolysis
T	thermal reaction
S.T.	shock tube
D.F.	diffusion flame
M.D.F.	modified diffusion flame
M.L.	mean life method
Dil. F.	dilute flame
M.B.	molecular beam
+H	Hg photosensitized addition of H atoms to olefines.
−H	Hg photosensitized removal of H atoms from saturated compounds.
$+CH_3$	CH_3 radical attack on the parent compound.

The other radical source abbreviations used, such as H_2/discharge and H_2/O_2 flame, are self explanatory.

The table for each attacking species R_1 is split into six sections defined by the atom X being transferred. In the order used in the tables these are:

(i) hydrogen atom transfer
(ii) fluorine atom transfer
(iii) chlorine atom transfer
(iv) bromine atom transfer
(v) iodine atom transfer
(vi) oxygen atom transfer

Only in the case of methyl radicals are all six categories used.

In the few cases not covered by this classification e.g., transfer of an atom from the radical to the molecule as in

$$HO_2 + CO = CO_2 + OH,$$

either the reaction is written in full, or the products of the reaction are indicated in a footnote.

A seventh category of reactions not already covered (e.g., group transfer and inversion reactions) is included at the end of each table.

Simple ratios of rate constants (of the form k_1/k_2) are presented in separate tables, these proved much more difficult to classify, and wherever necessary, explanations of the construction of these tables are included at the head of the table.

Rate data is available in the literature as complex functions of several rate constants: this data has not been included, but references as to where it is available are given at the appropriate sections in the tables.

Where data is considered to be doubtful this is indicated in a footnote. As far as possible, an attempt has been made to include criticism of data by cross reference. Thus, where several references are given for one set of Arrhenius values, the first reference contains the values themselves; the other references indicate the sources of supplementary data and/or comment on the values shown.

Where a sufficient quantity of data has been collected for any one reaction, recommended Arrhenius values are given. They are compatible in all cases with the values for the reverse reaction (where these are known).

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Reaction of Hydrogen Atoms

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Metathetical Reactions of Hydrogen Atoms With Hydrogen

Reactions	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$H+H_2$	(a)	6.68	13.78			1
	(b)	7.5 ± 1	13.7	10–730		2
	(d) (c)	8.0 ± 0.5	14.05	10–730		8
		$\log_{10} k=15.45-3.49\times10^3/T+3.84\times10^5/T^2$		27–171	H_2/tungsten spiral	11
	(e) (f)	$k=1.18\times10^{15}T^{-1/2}\Gamma\exp(-9.21\times10^3/RT)$		27–171	H_2/tunsgten spiral	12
$H+\mathbf{H}D$	(a)	6.96	13.12			1
$H+H\mathbf{D}$	(a)	7.04	13.06			1
$H+D_2$	(a)	7.48	13.32			1
		7.30 ± 0.1	12.64 ± 0.05	95–195	H_2/tungsten spiral	13
$D+H_2$	(a)	6.14	13.37			1
	(f)	$k=3.63\times10^{15}T^{-1/2}\Gamma\exp(-9.40\times10^3/RT)$		1–195	D_2/tungsten spiral	12
$D+\mathbf{H}D$	(a)	6.40	12.99			1
$D+H\mathbf{D}$	(a)	6.48	12.93			1
$D+D_2$	(a)	6.09	13.49			1

Notes

(a) A self-consistent set of values derived from absolute rate calculations.

(b) Review of literature data (refs. 3 to 6).

(c) Review of literature data (refs. 3 to 7).

(d) For a critical summary of the (then) available experimental data, see refs. 9 and 10.

(e) Recalculation of the data from ref. 11.

(f) Γ is the tunneling factor.

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Metathetical Reactions of Hydrogen Atoms

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
		HYDROGEN ATOM TRANSFER				
Alkanes						
CH_4	(a)	7.0 ± 1.5		130–290		1
		6.6	10.5	99–163	H_2/tungsten filament	2
		4.5 ± 1.2	10.01 ± 0.2	99–163	H_2/tungsten filament	3

Metathetical Reactions of Hydrogen Atoms—Continued

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
	(a)	9.0	12.5	130–420		4
	(a)	8.0	12.6	477–547		5
		11.5	14.3	950–1530	CH_4/O_2 flame	6
		15.1	14.53	400–480	H_2/O_2 ignition	7
	(b)	11.05	14.19			8
		$k=2.9\times10^{10}$		610	H_2/O_2 ignition	9
		7.4 ± 1.1	11.8	212–530	H_2/discharge	10
		8.0	13.9	697–863	H_2O_2 ignition	11
	(w) (q)	13.5		450	D_2/discharge	12
	(w) (c)	7.8	13.0	347–465	D_2CO photolysis	13
	(r)	9.6	12.6			
C_2H_2	(d)	1.5				14
C_2H_4	(e)	6.6 ± 1	13.26	500–625	H_2/O_2 ignition	15
C_2H_6		6.8	12.53	80–163	H_2/tungsten filament	16
		12.0	13.17	410–550	H_2O_2 ignition	17
	(e)	14 ± 1	14.76	500–625	H_2/O_2 ignition	15
	(q)	9.0 ± 0.2		24 ± 2	H_2/discharge	18
		12.2	14.52	410–550	H_2/O_2 ignition	7
	(f)	9.9 ± 1.0	14.20 ± 0.4	25–1230		19
		9.7 ± 2	14.1	720–1160	$C_2H_6/H_2/O_2$ flame	105
	(g)	$k=3.0\times10^{9}$		630		20
	(h)	9.0	13.5	50–250	C_2H_6/C_3H_6 radiolysis	21
	(f)	9.71 ± 0.58	14.12 ± 0.25	31–1227		22
		6.20	13.6	752–917	H_2/O_2 ignition	11
	(w) (i)	9.0	14.4	30–306	D_2S/C_2H_6 photolysis	23
C_3H_6	(e)	1.1 ± 1	12.45	500–625	H_2/O_2 ignition	15
	(w) (i)	5.0	13.7	25–205	$D_2S+C_3H_6$ photolysis	23
C_3H_8		8.5	13.43	410–550	H_2/O_2 ignition	17
	(e)	8.3 ± 1	13.56	500–625	H_2/O_2 ignition	15
		8.8	13.80	410–550	H_2/O_2 ignition	7
	(h)	7.4	13.7	57–217	C_3H_8 radiolysis	24
		8.2	14.12	95–170	H_2/tungsten filament	25
	(j)	$k=4.53\times10^{11}$		520	H_2/O_2 ignition	26
	(f)	7.83 ± 0.79	13.81 ± 0.37	28–520		26
	(w) (q)	8.0		Room temp.	H_2/discharge	27
	(w) (i)	7.2	14.5	30–250	$D_2S+C_3H_8$ photolysis	23
$CH_3CH{:}CHCH_3$	(w) (i)	5.0	14.1	28–230	$D_2S+C_4H_8$ photolysis	23
n-C_4H_{10}	(q)	8.9		Room temp.	H_2/discharge	27
	(j)	$k=5.1\times10^{11}$		520	H_2/O_2 ignition	28
	(f)	7.5 ± 0.5	13.9 ± 0.2	27–520		28
	(h)	6.7	13.3	50–250	$n-C_4H_{10}$ radiolysis	21
	(k)	7.1	13.82	70–170	H_2/tungsten filament	29
	(w) (q)	7.9		Room temp.	H_2/discharge	27
	(w) (i)	7.1	14.5	30–250	$D_2S+C_4H_{10}$ photolysis	23
i-C_4H_{10}	(q)	9.3			H_2/discharge	30
		6.0	13.47	410–550	H_2/O_2 ignition	17
	(e)	5.6 ± 1	12.89	500–625	H_2/O_2 ignition	15
		5.1	12.76	410–510	H_2/O_2 ignition	7
	(h)	5.1	13.1	50–250	i-C_4H_{10} radiolysis	21
	(j)	$k=9.2\times10^{11}$		520	H_2/O_2 ignition	28

Metathetical Reactions of Hydrogen Atoms—Continued

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
	(f)	6.8 ± 0.5	14.0 ± 0.2	27–520		28
	(w) (i)	6.3	14.5	30–350	$D_2S + C_4H_{10}$ photolysis	23
n-C_5H_{12}	(q)	8.5		Room temp.	H_2/discharge	27
	(w) (q)	7.8		Room temp.	D_2/discharge	27
neo-C_5H_{12}	(q)	9.2		Room temp.	H_2/discharge	31
n-C_6H_{14}	(q)	9.1		Room temp.	H_2/discharge	27
	(f)	5.9		25–305		32
	(w) (q)	8.0		Room temp.	D_2/discharge	27
Cyclo Alkanes						
cyclo-C_3H_6	(q)	9.5		Room temp.	H_2/discharge	27
	(w) (q)	9.3		Room temp.	D_2/discharge	27
cyclo-C_4H_8	(q)	8.2		Room temp.	H_2/discharge	27
	(w) (q)	7.7		Room temp.	D_2/discharge	27
cyclo-C_6H_{10}	(q)	7.5		Room temp.	H_2/discharge	27
	(w) (q)	6.6		Room temp.	D_2/discharge	27
cyclo-C_6H_{12}	(q)	8.0		Room temp.	H_2/discharge	27
	(w) (q)	7.2		Room temp.	D_2/discharge	27
Aromatic hydrocarbons						
C_6H_6	(q)	< 7		Room temp.	H_2/discharge	27
	(w) (q)	< 6		Room temp.	D_2/discharge	27
Aldehydes and ketones						
HCHO	(l)	2.6	13.21	252–397	H_2CO/D_2 photolysis	33
	(f)	3.49	13.46	327–727		34
	(f)	3.26	13.29	250–400		34
		$k = (2.7 \pm 0.7) \times 10^{10}$		27	H_2/discharge	35
		$k = 3.5 \times 10^{12}$		547	HCHO pyrolysis	36
	(w) (l)	2.7	13.21	252–397	H_2CO/D_2 photolysis	33
DCDO	(l)	3.6	13.21	252–397	H_2CO/D_2CO photolysis	33
	(w) (m)	3.0	13.3	308–341	D_2CO photolysis	13
	(w) (l)	3.6	13.21	252–397	H_2CO/D_2CO photolysis	33
CH_3CHO	(q)	$\leqslant 6$		25	H_2/discharge	37
CH_3COCH_3	(q)	8.8		Room temp.	H_2/discharge	38
	(w) (q)	8.0		Room temp.	D_2/discharge	38
Metal alkyl						
CH_3HgCH_3	(q)	$\leqslant 6$		25	H_2/ discharge	106
Halogenated methane						
CF_3H	(a)	5.0	12.7	832–1011	H_2/O_2 ignition	11

Metathetical Reactions of Hydrogen Atoms—Continued

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
Hydrogen halides						
H F	(n)	35.0	13.00	3527–5027	HF shock wave decomposition	39
H Cl		5.2	13.4	628–798	H_2/HCl thermal reaction	40
	(a)	4.5				41
H Br		2.2	13.79	832–1011	H_2/O_2 ignition	11
		0.9	13.1	548–711	H_2/HBr thermal reaction	42
	(o)	3.7	14.04	700–1400		43
	(r)	2.9	13.8			
HI		0.7 ± 0.25	13.70 ± 0.07	394–527	H_2/I_2 thermal reaction	44
		1.17 ± 0.35	13.8 ± 0.2	394–465	H_2/I_2 thermal reaction	107
Hydrides of oxygen and nitrogen						
H_2O		$k = 6.6 \pm 0.9 \times 10^9$		799	$H_2/O_2/N_2O$ flame	45
	(a)	20.4	13.96	37–642		108
	(a)	21.6	14.84	687–807	H_2/O_2 ignition	46
	(f)	21.1 ± 1.5	14.48 ± 1.0	27–1727		47
D_2O	(a)	25.5	15	1012–1227		109
		$k = 5.0 \times 10^9$		799	H_2/O_2 flame	48
		$k = 3.6 \times 10^9$		799	H_2/O_2 flame	49
	(p) (f)	21.8	13.93	799	H_2/O_2 flame	45
H_2O_2	(a)	18.8	16.39	687–807	H_2O_2 ignition	46
N_2H_4		2.0	11.54	25–150	H_2/ discharge	50
			FLUORINE ATOM TRANSFER			
SF_6		30 ± 5	15.3	1030–1670	H_2/O_2 and C_2H_2/O_2 flames	51
			CHLORINE ATOM TRANSFER			
HCl		0.9 ± 1.3		22–152	HCl/D_2 and DCl/H_2 photolysis	52
Cl_2		> 2.1		25–75	$H_2/Cl_2/O_2$ photolysis	53
		> 2.9				54
		> 1.8		25–100	$H_2/Cl_2/O_2$ photolysis	55
		> 1.6		0–85	$H_2/Cl_2/O_2$ photolysis	56
		< 2.5				57
CCl_4	(s)	~ 5		2034	Molecular beam	58

Metathetical Reactions of Hydrogen Atoms – Continued

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
BROMINE ATOM TRANSFER						
Br_2		3.7	14.97	700–1400		43
CF_3Br		17.45	15.64	832–1011	H_2/O_2 ignition	11
$C_2F_4Br_2$		14.5	16.0	855–1013	H_2/O_2 ignition	11
IODINE ATOM TRANSFER						
I_2		0.0 ± 0.5	14.6 ± 0.2	394–465	H_2/I_2 thermal reaction	107
OXYGEN ATOM TRANSFER						
O_2		$k = 5.0 \times 10^9$		485	H_2/O_2 ignition	60
		$k = 6.7 \times 10^9$		520	H_2/O_2 ignition	60
		$k = 2.7 \times 10^9$		520	H_2/O_2 ignition	61
		$k = 6.6 \times 10^8$		520	H_2/O_2 ignition	62
		15.1	13.75		H_2/O_2 ignition	63
		$k = 1.43 \times 10^{12}$		1380	H_2/O_2 ignition	64
		20.0 ± 2.0	14.9	1012–1227	H_2/O_2 flame	109
		$k = 1.5 \times 10^{11}$		827	H_2/O_2 flame	110
	(t)	14.9	13.72		H_2/O_2 ignition	65
		15.9 ± 0.8	13.89	570–660	$H_2/CO/O_2$ ignition	66
		$k = 6.0 \times 10^9$		540	H_2/O_2 ignition	34
		15.0 ± 0.6	13.59	590–660	$C_2H_6/CO/O_2$ ignition	111
		16.3		552–1089	H_2/O_2 ignition	67
		17.4 ± 0.7	14.82 ± 0.2	1853–2772	H_2/O_2 flame	68
	(a)	$k = 1.83 \times 10^3$		20		69
	(a)	$k = 3.28 \times 10^3$		37		70
	(f)	17.8 ± 1.0	15.08 ± 0.8	27–327		70
	(f)	16.9 ± 1.0	14.86 ± 0.8	1227–1427		70
		18.9 ± 0.9		620–1080	H_2/O_2 ignition	71
		15.6 ± 0.6	13.66	570–660	$H_2/CO/O_2$ ignition	72
	(f)	16.49 ± 0.70	14.31 ± 0.28	20–1377		73
		17.0	13.69	999–1923	C_2H_2/O_2 oxidation	74
		17.75	15.0	687–807	H_2/O_2 ignition	46
		$k = 1.6 \times 10^{10}$		642	H_2/O_2 flame	108
	(f)	16.50	14.34	20–1400		112
O_3		$k = (2.4 \pm 0.3) \times 10^{12}$		Room temp.	Diffusion flame	75
		$k = (1.6 \pm 0.3) \times 10^{12}$		Room temp.	H_2 discharge	76
H_2O_2	(u)	$k = (1.9 - 3.0) \times 10^{11}$		447	H_2O_2 ignition	77
	(u)	$k = 1.1 \times 10^{12}$		500	H_2/O_2 slow reaction	78
N_2O		16.3 ± 2.0	14.62	990–1510	$H_2/N_2O/O_2$ flame	110
		$k = 4.3 \times 10^{10}$		627	$H_2/N_2O/O_2$ flame	108
		$k = 2.9 \times 10^{11}$		1084	$H_2/N_2O/O_2$ flame	108
		$k = (4.3 \pm 1.5) \times 10^{10}$		627	$H_2/N_2O/O_2$ flame	45
	(f)	13 ± 1.5	13.7 ± 0.4	150–1487		45

Metathetical Reactions of Hydrogen Atoms—Continued

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(kcal mole⁻¹)	*(cm³ mole⁻¹ sec⁻¹)*	°C		
NO_2		$k=3.2\times 10^{13}$		227–267	H_2/Cl_2NO_2 thermal reaction	79
		$k=2.9\times 10^{13}$		25	H_2/ discharge	80
		$k=(2.9\pm 0.3)\times 10^{13}$		Room temp.	H_2/ discharge	76
	(v)	$k=5.5\times 10^{13}$		360	H_2/O_2 ignition	81
CO_2		33.3	15.48	944–1072	H_2/O_2 flame	113
	(b)	29.7	14.89	1000–1500		8
		$k=8.4\times 10^{8}$		799	H_2/O_2 flame	49

Ratios of Rate Constants (Hydrogen Atoms)

(i) Reactions of the type (1) $H+RH=H_2+R$ where RH is any hydrogen containing compound.
(2) $H+OL=OLH$ where OL is an olefine.

RH	OL	Notes	k_1/k_2	E_1-E_2	$\log_{10} A_1/A_2$	Temperature range	Radical source	Reference
				(kcal mole⁻¹)		°C		
CH_4	C_2H_4		2.6×10^{-6}			120	CH_4 -H	82
C_2H_4	C_2H_4		-1.0×10^{-3} (i.e. $=0$)			24	n-C_4H_{10} -H	83
C_2H_6	C_2H_4		2.5×10^{-5}			25	C_2H_6 radiolysis	84
C_3H_6	C_3H_6		4.5×10^{-2}			24	n-C_4H_{10} -H	83
			$(4.10\pm 0.37)\times 10^{-2}$			25	n-C_4H_{10} -H	85
C_3D_6	C_3D_6		$(6.3\pm 2.3)\times 10^{-2}$			25	n-C_4H_{10} -H	85
C_3H_8	C_2H_4		1.9×10^{-3}			25	C_3H_8 -H	86
			1.5×10^{-3}			24	C_3H_8 -H	87
C_3H_8	C_3H_6		5.2×10^{-4}			25	C_3H_8 radiolysis	88
1,3-C_4H_6	1,3-C_4H_6		3.2×10^{-2}			24	n-C_4H_{10} -H	83
1-C_4H_8	1-C_4H_8		8.1×10^{-2}			24	n-C_4H_{10} -H	83
i-C_4H_8	i-C_4H_8		2.0×10^{-2}			24	n-C_4H_{10} -H	83
cisC_4H_8-2	cisC_4H_8-2		6.6×10^{-2}			24	n-C_4H_{10} -H	83
transC_4H_8-2	transC_4H_8-2		11.7×10^{-2}			24	n-C_4H_{10} -H	83
n-C_4H_{10}	C_3H_6		1.4×10^{-3}			25	n-C_4H_{10} -H	85
n-C_4H_{10}	C_3D_6		1.3×10^{-3}			25	n-C_4H_{10} -H	85
i-C_4H_{10}	C_2H_4		8.6×10^{-3}			25	i-C_4H_{10} -H	86
			8.1×10^{-3}			24	i-C_4H_{10} -H	87

Ratios of Rate Constants Hydrogen Atoms)—Continued

RH	OL	Notes	k_1/k_2	E_1-E_2	$\log_{10} A_1/A_2$	Temperature range	Radical source	Reference
				(*kcal mole*$^{-1}$)		°C		
cyclo-C_5H_{10}	cyclo-C_5H_8		5.7×10^{-3}			24	cyclo-C_5H_{10} -H	89
n-C_5H_{12}	C_2H_4		3.7×10^{-3} 2.2×10^{-3}			25 24	n-C_5H_{12} -H n-C_5H_{12} -H	86 87
n-C_5H_{12}	C_5H_{10}	(y)	$\geqslant 4.5\times10^{-3}$			21	n-C_5H_{12} -H	114
i-C_5H_{12}	C_2H_4		10.6×10^{-3}			25	i-C_5H_{12} -H	86
$(CH_3)_2C{:}C(CH_3)_2$	$(CH_3)_2C{:}C(CH_3)_2$		-2.5×10^{-2} (i.e. $=0$)			24	n-C_4H_{10} -H	83
n-C_6H_{14}	C_2H_4		3.7×10^{-3}			25	n-C_6H_{14} -H	86
neo-C_6H_{14}	C_2H_4		1.8×10^{-3}			25	neo-C_6H_{14} -H	86
$(CH_3)_2CHCH_2CH_2CH_3$	C_2H_4		11.6×10^{-3}			25	$(CH_3)_2CHCH_2CH_2CH_3$ -H	86
$(CH_3)_2CHCH(CH_3)_2$	C_2H_4		21.0×10^{-3}			25	$(CH_3)_2CHCH(CH_3)_2$ -H	86
H_2S	C_2H_4		0.5			30	H_2S photolysis	90
CH_3SH	C_2H_4			0.54 ± 0.12	0.59	50–220	CH_3SH photolysis	91

(ii) Miscellaneous reactions of hydrogen atoms with hydrocarbons and hydrocarbon derivatives.

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°C		
(1) $H+CCl_3D=CCl_3+HD$ (2) $H+CCl_3D=CCl_2D+HCl$				1.1	Room temp.	H_2/ discharge	92
(1) $H+CCl_3Br=CCl_3+HBr$ (2) $H+CCl_3Br=CCl_2Br+HCl$				0.49	Room temp.	H_2/ discharge	115
(1) $H+CCl_3F=CCl_3+HF$ (2) $H+CCl_3F=CCl_2F+HCl$				0.071	Room temp.	H_2/ discharge	115
(1) $H+CCl_2BrH=CCl_2Br+H_2$ (2) $H+CCl_2BrH=CClBrH+HCl$				1.7	Room temp.	H_2/ discharge	92
(1) $H+CCl_2BrH=CCl_2H+HBr$ (2) $H+CCl_2BrH=CClBrH+HCl$				0.8	Room temp.	H_2/ discharge	92
(1) $H+C_3H_6=C_3H_5+H_2$ (2) $H+C_3H_8=C_3H_7+H_2$				32	25	C_3H_8 radiolysis	88
(1) $H+(CH_3)_3CD=C_4H_9+HD$ (2) $H+(CH_3)_3CD=C_4H_8D+H_2$				1.2	25	i-C_4H_9D photolysis	93

Ratios of Rate Constants (Hydrogen Atoms) – Continued

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°*C*		
(1) $D+(CH_3)_3CD=C_4H_9+D_2$ (2) $D+(CH_3)_3CD$ $=C_4H_8D+HD$				1.2	25	i-C_4H_9D photolysis	93
(1) $H+i$-C_5H_{12} $=C_5H_{11}+H_2$ (2) $H+C_5H_{11}=C_5H_{10}+H_2$	(z)			5.2×10^{-2}	25	i-C_5H_{12}-H	94
(1) $H+1$-$C_5H_{10}=C_5H_9+H_2$ (2) $H+n$-$C_5H_{12}=C_5H_{11}+H_2$				8.8	21	n-C_5H_{12}-H	88
(1) $H+i$-$C_5H_{12}=C_5H_{11}+H_2$ (2) $H+C_5H_{11}=C_5H_{12}$	(z)			5.9×10^{-3}	25	i-C_5H_{12}-H	94
(1) $H+n$-$C_6H_{14}=C_6H_{13}+H_2$ (2) $H+C_6H_{13}=C_6H_{14}$				5.3×10^{-3} 1.3×10^{-3}	25 25	n-C_6H_{14}-H n-C_6H_{14}/1-C_6H_{12}-H	94 94
(1) $H+CH_3CH{:}CHCHO$ $=CH_3CH{:}CHCO+H_2$ (2) $H+CH_3CH{:}CHCHO$ $=CH_3CH{:}CH_2+HCO$		~0.5			210–350	$(CH_3)_2CO$/ $CH_3CH{:}CHCHO$ photolysis	95

(iii) Reactions of the type (1) $H+HX=H_2+X$
(2) $H+X_2=HX+X$ where X is a halogen

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
(1) $H+HCl=H_2+Cl$				≤ 0.05	25	H_2/Cl_2 photolysis	96
(2) $H+Cl_2=HCl+Cl$		1.54 ± 0.13	−0.84 ± 0.1		0–62	H_2/Cl_2 photolysis	97
(1) $H+HBr=H_2+Br$	(aa)			0.12	327–1197	H_2/Br_2 thermal reaction	98
(2) $H+Br_2=HBr+Br$				0.1	162–310	H_2/Br_2 photolysis	99
				0.12 ± 0.009	25–300	H_2/Br_2 thermal reaction	100
				0.099 ± 0.007	1027–1427	H_2/Br_2 thermal reaction	101
(1) $H+HI=H_2+I$				0.070 ± 0.02	394	H_2/I_2 thermal reaction	44
(2) $H+I_2=HI+I$				0.082 ± 0.012	527	H_2/I_2 thermal reaction	44
				0.06	700		102
(1) $D+DI=D_2+I$ (2) $D+I_2=DI+I$				0.073	527	D_2/I_2 thermal reaction	116

(iv) Miscellaneous Ratios

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
(1) $H+D_2=HD+D$ (2) $H+HCl=H_2+Cl$				14 ± 4	22	HCl/D_2 photolysis	52
(1) $D+HD=D_2+H$ (2) $D+DCl=D_2+Cl$				65	22	H_2/DCl photolysis	52
(1) $D+HCl=HD+Cl$				0.5 ± 0.4	22		52
(2) $D+HCl=DCl+H$				5. ± 4	152	D_2/HCl photolysis	52

Ratios of Rate Constants (Hydrogen Atoms)—Continued

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°*C*		
(1) $H+D_2=HD+D$ (2) $H+HBr=H_2+Br$				0.55	22	D_2/HBr photolysis	52
(1) $H+NO_2=NO+OH$ (2) $H+Cl_2=HCl+Cl$		−3.13	0.42		227–267	$H_2/Cl_2/NO_2$ thermal reaction	79
(1) $D+C_2H_6=C_2H_5+HD$ (2) $D+DI=D_2+I$				1.2×10^{-3} 8.7×10^{-3}	25 100	DI photolysis DI photolysis	103 103
(1) $H+H_2S=HS+H_2$ (2) $H+O_2=HO_2$				0.60 0.137 0.171	50 93 100	H_2S photo-oxidation	104

Notes

(a) Estimated from the reverse reaction.

(b) This value was used by the authors in the region 1000–1500 °C, but its origin was not stated.

(c) Measured relative to $D+D_2CO=D_2+DCO$ for which $k=10^{13.30}\exp(-3000\ RT)$.

(d) Private communication from Asaba.

(e) Taken from Tikhomirova and Voevodsky, "Chain oxidation of Hydorcarbons in the Gas Phase" (Russ), Moscow, 1955.

(f) Critical survey of literature data.

(g) "A rough estimate."

(h) Measured relative to $H+C_3H_6=C_3H_7$ for which $k=10^{13.5}\exp(-2600/RT)$.

(i) Measured relative to $D+H_2=HD+H$ for which $k=10^{13.4}\exp(-5000/RT)$.

(j) Measured relative to $H+O_2=OH+O$ for which $k=5.1\times10^9$ at 520 °C.

(k) Measured relative to $H+C_3H_8=C_3H_7+H_2$ for which $k=10^{14.11}\exp(-8200/RT)$.

(l) Measured relative to $D+H_2=HD+H$ for which $k=10^{13.92}\exp(-6000/RT)$.

(m) Measured relative to $D+H_2=HD+H$ for which $k=10^{13.46}\exp(-5400/RT)$.

(n) Rate constant estimated in computer calculations. *E* value assumed and *A* factor varied.

(o) Estimated from kinetic data.

(p) The value of *E* was assumed, and *A* calculated from the rate constant.

(q) A steric factor of 0.1 was assumed.

(r) Calculated from the recommended value for the reverse reaction.

(s) Steric factor$=0.13$.

(t) Used at flame temperatures.

(u) Measured relative to $H+O_2=OH+O$ for which $k=10^{14.31}\exp(-16500/RT)$.

(v) Measured relative to $H+O_2+H_2=HO_2+H_2$ for which $k=5.5\times10^{15}$ cm^6 mole^2 sec^{-1}

(w) Reactions with D atoms.

(x) Calculated from the recommended value for the reverse reaction.

(y) C_5H_{10} refers to the mixture of pentenes formed in the primary reaction.

(z) C_5H_{11} is a radical formed in the primary process, probably either $CH_3C(CH_3)CH_2CH_3$ or $CH_3CH(CH_3)CHCH_3$.

(aa) The author shows that this value is compatible with his results in the temperature range shown.

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Metathetical Reactions of Fluorine Atoms

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
Hydrogen		*(kcal mole^{-1})*	*(cm^3 mole^{-1} sec^{-1})*	°C		
H_2	(a)	1.71 ± 0.22	14.07	25–150	$CH_4/H_2/F_2$ P	1, 4
Alkanes						
CH_4	(a)	1.21 ± 0.80	14.09	−75–78	$CH_4/C_2H_6/F_2$ T	2, 4
C_2H_6		0.28	13.78	−60–20	standard T	2, 4
$\mathbf{CH}_3CH_2\mathbf{CH}_3$	(a)	0.00 ± 0.25	13.52	−60–20	$C_2H_6/C_3H_8/F_2$ T	2, 4
$CH_3\mathbf{CH}_2CH_3$	(a)	0.00 ± 0.25	13.10	−60–20	$C_2H_6/C_3H_8/F_2$ T	2, 4
$\mathbf{CH}_3CH_2CH_2\mathbf{CH}_3$	(a)	0.00 ± 0.70	13.46	−60–20	n-$C_4H_{10}/C_3H_8/F_2$ T	2, 3, 4
$CH_3\mathbf{CH}_2\mathbf{CH}_2CH_3$	(a)	0.00 ± 0.65	13.37	−60–20	n-$C_4H_{10}/C_3H_8/F_2$ T	2, 3, 4
$(\mathbf{CH}_3)_3CH$	(a)	0.00 ± 0.70	13.65	−60–20	n-C_4H_{10}/i-C_4H_{10}/F_2 T	2, 3, 4
$(CH_3)_3\mathbf{CH}$	(a)	0.00 ± 0.80	12.84	−60–20	n-C_4H_{10}/i-C_4H_{10}/F_2 T	2, 3, 4
$(CH_3)_4C$	(a)	0.00 ± 0.80	13.75	−60–20	i-$C_4H_{10}/(CH_3)_4C/F_2$ T	2, 4
Cyclo-Alkane						
cyclo-C_3H_6	(a)	0.00 ± 0.10	13.46		cyclo-$C_3H_6/C_3H_8/F_2$ T	2, 4
CHLORINE ATOM TRANSFER						
CCl_4		$k = 2 \times 10^{13}$		20	CCl_4/F_2 T	5
OXYGEN ATOM TRANSFER						
O_3		2.8		0–20	F_2/O_3 P	6

Notes

(a) These values are based on the assumed value $k = 10^{13.78} \exp(-280/RT)$ for the reaction $F + C_2H_6 = C_2H_5 + HF$.

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Reaction of Chlorine Atoms

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Reaction with

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Reaction with

Metathetical Reactions of Chlorine Atoms

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source		References
			HYDROGEN ATOM TRANSFER				
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*			
Hydrogen							
H_2		$\geqslant 5.9$		25–75	H_2/Cl_2	P	1
		$\geqslant 5.8$		−73–23	H_2/Cl_2	P	2
		6.1 ± 1.0	14.3	0–25	Cl_2 discharge		3, 38
		$k = (4.8 \pm 0.4) \times 10^{11}$		250	$H_2/Cl_2/NO$	T	5, 6
		5.9		628–798	H_2/HCl	T	4
	(a)	5.48 ± 0.14	13.92 ± 0.03	0–798			7, 5
		5.48	13.92				
HD	(b)	5.97	13.83	−33–77	$H_2/HD/Cl_2$	P	8, 41
HT	(b)	6.03	13.79	−38–72	$H_2/HT/Cl_2$	P	9
	(b)	6.28	13.82	−30–70	$H_2/HD/HT/Cl_2$	P	41
D_2	(b)	6.60	13.78	0–32	$H_2/CO/Cl_2$	P	10, 11, 7
	(b)	6.70	13.84	30–178	$H_2/D_2/Cl_2$	P	12
	(b)	6.61	13.76	−30–70	$HD/D_2/Cl_2$	P	41
DT	(b)	6.90	13.73	−30–70	$DT/D_2/Cl_2$	P	41
T_2	(b)	7.17	13.73	−30–70	$T_2/D_2/Cl_2$	P	41
Alkanes							
CH_4	(b)	3.85 ± 0.18	13.42	20–211	$CH_4/H_2/Cl_2$	P	13, 16
CD_4	(i)	5.76	13.73	31–188	$CH_4/CD_4/Cl_2$	P	12
C_2H_6	(b)	1.04 ± 0.08	13.96	−41–385	$CH_4/C_2H_6/Cl_2$	P	14, 15
	(b)	1.00	14.08	76–290	$CH_4/C_2H_6/Cl_2$	P	16
C_2D_6	(i)	1.32	13.75	30–160	$C_2H_6/C_2D_6/Cl_2$	P	12
C_3H_8	(b)	0.67	14.28	25–211	$C_3H_8/C_2H_6/Cl_2$	P	16
$C\mathbf{H}_3CH_2C\mathbf{H}_3$	(b)	0.98	14.03	−70–230	$C_2H_6/C_3H_8/Cl_2$	P	14, 15
$CH_3C\mathbf{H}_2CH_3$	(b)	0.66	13.87	−70–230	$C_2H_6/C_3H_8/Cl_2$	P	14, 15
$C\mathbf{H}_3CH_2CH_2C\mathbf{H}_3$	(b)	0.77	13.93	−70–200	$C_2H_6/n\text{-}C_4H_{10}/Cl_2$	P	14, 17
$CH_3C\mathbf{H}_2C\mathbf{H}_2CH_3$	(b)	0.25	13.95	−70–200	$C_2H_6/n\text{-}C_4H_{10}/Cl_2$	P	14, 17
$(CH_3)_3CH$	(b)	0.86	14.29	25–211	$C_2H_6/i\text{-}C_4H_{10}/Cl_2$	P	16
$(C\mathbf{H}_3)_3CH$	(b)	0.80	14.09	−80–100	$C_2H_6/i\text{-}C_4H_{10}/Cl_2$	P	14, 17
$(CH_3)_3C\mathbf{H}$	(b)	0.02	13.24	−80–100	$C_2H_6/i\text{-}C_4H_{10}/Cl_2$	P	14, 17
$(CH_3)_4C$	(b)	0.90	14.25	−70–230	$C_3H_8/(CH_3)_4C/Cl_2$	P	14
	(b)	0.70	14.09	25–211	$C_2H_6/(CH_3)_4C/Cl_2$	P	16
Cyclo-alkanes							
cyclo-C_3H_6	(b)	4.12	13.73	20–260	C_2H_6/cyclo-C_3H_6/Cl_2	P	14

Metathetical Reactions of Chlorine Atoms—Continued

Reactants	Notes	E	log$_{10}$ A	Temperature range	Radical source		References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C			
cyclo-C_4H_8	(b)	0.80	14.43	−30–105	C_3H_8/cyclo-C_4H_8/Cl_2	P	14
cyclo-C_5H_{10}	(b)	0.58	14.47	25–211	C_2H_6/cyclo-C_5H_{10}/Cl_2	P	16
Halogenated alkanes							
CH_3Cl	(b)	3.36	13.76	25–211	CH_4/CH_3Cl/Cl_2	P	16
	(b)	3.3 ± 0.1	13.5 ± 0.7	0–300	CH_3Cl/various RH/Cl_2 P	P	18
	(c)	3.08	13.5	85–180	C_2Cl_4/CH_3Cl/Cl_2	P	19
CH_2Cl_2		5.5	14.6				28
		3.0	13.43	0–300	CH_2Cl_2/various RH/Cl_2 P	P	18
	(c)	3.12	13.4	110–210	C_2Cl_4/CH_2Cl_2/Cl_2	P	19
$CHCl_3$		6.5	14.6				28
		3.35	12.84	0–300	CH_4/$CHCl_3$/Cl_2	P	18, 27
	(c)	3.33	13.2	140–210	C_2Cl_4/$CHCl_3$/Cl_2	P	19, 20, 21
$CDCl_3$	(d)	4.06 ± 0.2	12.69	−20–180	$CHCl_3$/$CDCl_3$/Cl_2	P	22
	(d)	4.79	13.30	109–203	$CHCl_3$/$CDCl_3$/Cl_2	P	12
C_2H_5Cl	(b)	1.50 ± 0.2	13.66	25–211	C_2H_6/C_2H_5Cl/Cl_2	P	16
CH_2ClCH_2Cl		3.0	13.4				23
$C_2H_3Cl_3$		3.5	13.5				23
$CHCl_2CHCl_2$		3.3	13.8				23
C_2HCl_5		5.4	13.9				28
		3.3	12.8	110–210	C_2Cl_4/C_2HCl_5/Cl_2	P	19, 24
		3.4	12.7				18
$CH_3CH_2CH_2C\mathbf{H}_2F$	(e)	0.77 ± 0.10	13.0	0–230	C_4H_9F/Cl_2	P	25, 26, 29
$CH_3CH_2C\mathbf{H}_2CH_2F$	(e)	0.62 ± 0.15	13.1	0–230	C_4H_9F/Cl_2	P	25, 26, 29
$CH_3C\mathbf{H}_2CH_2CH_2F$	(e)	(0.37 ± 0.10)	(13.3)	0–230	C_4H_9F/Cl_2	P	25, 26, 29
$C\mathbf{H}_3CH_2CH_2CH_2F$	(e)	0.77	13.1	0–230	C_4H_9F/Cl_2	P	25, 26, 29
$CH_3CH_2CH_2C\mathbf{H}_2Cl$	(e)	0.77 ± 0.20	13.4	35–146	C_4H_9Cl/Cl_2	P	26, 29
$CH_3CH_2C\mathbf{H}_2CH_2Cl$	(e)	0.30 ± 0.40	13.3	35–146	C_4H_9Cl/Cl_2	P	26, 29
$CH_3C\mathbf{H}_2CH_2CH_2Cl$	(e)	0.22 ± 0.10	13.7	35–146	C_4H_9Cl/Cl_2	P	26, 29
$C\mathbf{H}_3CH_2CH_2CH_2Cl$	(e)	(0.77)	(13.4)	35–146	C_4H_9Cl/Cl_2	P	26, 29
$CF_3C\mathbf{H}_2CH_2CH_2CH_3$	(e)	2.0	12.2	0–230	$CF_3C_4H_9$/Cl_2	P	25
$CF_3CH_2C\mathbf{H}_2CH_2CH_3$	(e)	0.6	13.0	0–230	$CF_3C_4H_9$/Cl_2	P	25

Metathetical Reactions of Chlorine Atoms—Continued

Reactants	Notes	E	log₁₀ A	Temperature range	Radical source	References
		(kcal mole⁻¹)	*(cm³ mole⁻¹ sec⁻¹)*	°C		
$CF_3CH_2CH_2CH_2CH_3$	(e)	(0.3)	(13.3)	0–230	$CF_3C_4H_9/Cl_2$ P	25
$CF_3CH_2CH_2CH_2CH_3$	(e)	0.5	12.8	0–230	$CF_3C_4H_9/Cl_2$ P	25
Hydrogen Halide						
HCl		6.57 ± 0.49		39–150	$HCL/D_2/Cl_2$ P	39

CHLORINE ATOM TRANSFER

Reactants	Notes	E	log₁₀ A	Temperature range	Radical source	References
Halogenated alkanes						
CH_3Cl	(f) (g)	25.0	14.0			23, 30
CH_2Cl_2	(f) (g)	21.4	14.0			23, 30
$CHCl_3$	(f) (g)	21.0	14.0			23, 30
CCl_4	(f)	18.9	14.3			23
	(h)	20.0	14.0			28
C_2H_5Cl	(f)	21.5	14.3			23, 30
CH_2ClCH_2Cl	(f)	21.3	14.3			23, 30
$CHCl_2CH_2Cl$	(f)	20.6	14.3			23, 30
$CHCl_2CHCl_2$	(f)	20.4	14.3			23, 30
$CHCl_2CCl_3$	(h)	19.0	14.5			28
	(f)	18.3	14.3			23, 30
	(f)	17.9 ± 1.0	13.8 ± 0.5			31
C_2Cl_6	(f)	19.5	14.4			23
	(h)	18.0	13.5			28
Halogens and pseudo-halogens						
BrCl	(h)	1.1 ± 0.4	12.3	20–60		32
ICl		4.5	11.7	30–60	ICl P	33, 35
CNCl		34	14	1727–2527	ClCN S.T.	34
Carbonyls, etc.						
COCl		0.83	14.6	25–55	CO/Cl_2 P	36
$COCl_2$	(h)	19.9	14.4	25–55		28
	(a)	23.5	14.5	15–450		43

Metathetical Reactions of Chlorine Atoms—Continued

Reactants	Notes	*E*	$\log_{10} A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
NOCl		1.06	13.06	25–55	CO/NOCl/Cl_2 P	35
Cl_2O		$k > 4 \times 10^{11}$			Cl_2O F.P.	40
BROMINE ATOM TRANSFER						
Br_2		$k = (2.3 \pm 0.6) \times 10^{11}$		20	Br_2/Cl_2 P	32
OXYGEN ATOM TRANSFER						
N_2O		33.5	14.11	654–758	N_2O/Cl_2 T	37
MISCELLANEOUS REACTIONS						
$Cl + Na_2 = NaCl + Na$		$k = 1.5 \times 10^{14}$		~ 300	Na/Cl_2 D.F.	42

Notes

(a) Critical survey of literature data.

(b) Estimated assuming $k = 10^{13.92} \exp(-5480/RT)$ for the reaction $H_2 + Cl = HCl + H$.

(c) Activation energies are plotted to be in agreement with values found by Knox (ref. 18). The *A* factors are then adjusted to give the most consistent set of values for the rate constants.

(d) Calculated assuming $k = 10^{12.84} \exp(-3350/RT)$ *for the* reaction $CHCl_3 + Cl = CCl_3 + HCl$.

(e) The values at the δ or γ positions (bracketed) are assumed the same as for the 2 position in *n*-butane (ref. 14). The other values are calculated relative to this. These results must be considered very approximate.

(f) Estimated from thermodynamic data.

(g) *A* factor is assumed to be 10^{14}.

(h) Calculated from the reverse reaction.

(i) Estimated assuming $k = 10^{13.42} \exp(-3850/RT)$ for the *reaction* $CH_4 + Cl = CH_3 + HCl$.

(j) Estimated assuming $k = 10^{13.96} \exp(-1040/RT)$ for the reaction $C_2H_6 + Cl = C_2H_5 + HCl$.

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Metathetical Reactions of Bromine Atoms

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
HYDROGEN ATOM TRANSFER						
Hydrogen		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
H_2		19.4 ± 0.2	14.36	227–302	H_2/Br_2 T	1, 2
		18.6 ± 0.6	13.93	277–327	H_2/Br_2 T	3, 2
		17.6	13.86	200–300	H_2/Br_2 P	4
	(a)	19.8	13.36	700–1400		6
		$k=(0.89$ and $1.03) \times 10^{11}$		1123	H_2/Br_2 T	7
		$k=(0.91$ and $0.79) \times 10^{11}$		1168	H_2/Br_2 T	7
	(b)	17.8	13.7			18
		18.3	14.03	327–1197	H_2/Br_2 T	8
		19.2 ± 1.8	14.25	1027–1427	H_2/Br_2 T	2
	(b)	19.7 ± 0.4	14.43 ± 0.14	227–1427		9
		19.17	14.24	832–1011	$H_2/O_2/CF_3Br$ ignition	32
		19.7	14.43			
HD	(i)	20.3	14.37	168–350	$HD/H_2/Br_2$ T, P	34
HT	(i)	20.4	14.34	168–350	$HT/H_2/Br_2$ T, P	34
D_2		20.2	14.89	277–377	H_2/Br_2 T	3, 2
		20.4 ± 1.0	14.08	1027–1427	H_2/Br_2 T	2
	(i)	21.0	14.31	168–350	$H_2/D_2/Br$ T, P	34
	(b)	21.4 ± 0.4	14.29	277–1427		9
		21.4	14.29			
Alkanes						
CH_4		18.2 ± 0.5	13.8	150–210	CH_4/Br_2 P	10
	(c) (d)	18.3	14.0	204–341	$CH_4/CH_3Cl/Br_2$ T, P	11
		17.3	13.15	150–300		22
		18.2	13.8			
C_2H_6		13.6 ± 0.5		35–90	C_2H_6/Br_2 P	13
	(d)	13.4 ± 0.1	13.90 ± 0.04	59–199	$C_2H_6/CH_3Br/Br_2$ T	11, 14
	(e)	12.3	13.29	25–121	$CH_3CHF_2/C_2H_6/Br_2$ T	15
C_3H_8	(d)	10.15 ± 0.14	13.71 ± 0.07	13–145	$C_3H_8/C_2H_6/Br_2$ T	11, 14
n-C_4H_{10}	(d)	10.23 ± 0.23	13.22 ± 0.14	−6–98	n-C_4H_{10}/i-C_4H_{10}/Br_2 T	11, 14, 20
i-C_4H_{10}	(d)	7.51 ± 0.20	13.30 ± 0.11	34–148	i-$C_4H_{10}/C_3H_8/Br_2$ T	11, 14, 20
	(h)	11.7	17.6	40–95	i-C_4H_{10}/Br_2 P	16, 17
neo-C_5H_{12}	(d)	14.29 ± 0.13	14.24 ± 0.06	57–200	neo$C_5H_{12}/C_2H_6/Br_2$ T	11
	(h)	18.2	17.0	98–152	neo-C_5H_{12}/Br_2 P	19, 17
Aromatic hydrocarbon						
$C_6H_5CH_3$	(h)	7.6	13.5	82–132	$C_6H_5CH_3/Br_2$ P	21, 25, 17
Halogenated alkanes						
CH_3F	(e)	14.8	12.86	150–300	$CH_4/CH_3F/Br_2$ P	12
CH_2F_2	(e)	15.3	12.52	150–300	$CH_4/CH_2F_2/Br_2$ P	12

Metathetical Reactions of Bromine Atoms – Continued

Reactants	Notes	*E*	$\log_{10}A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
CHF_3	(e)	21.1	12.28	150–300	$CHF_3/C_2F_5H/Br_2$ P	12
		23.0	13.46	361–431	CF_3H/Br_2 T	22
CH_3Cl		14.45 ± 0.16	13.62 ± 0.06	59–200	$CH_3Cl/C_2H_6/Br_2$ T, P	11
$CHCl_3$		9.3	12.36	147–182	$CHCl_3/Br_2$ T	23, 17
		10.			$CHCl_3/Br_2$ P	24
CH_3Br		16.05	13.7	150–230	CH_3Br/Br_2 P	10, 11, 14
$CH_3C\mathbf{H}_2F$	(e)	10.3	12.38	39–121	$C_2H_6/C_2H_5F/Br_2$ P	15
$CH_3C\mathbf{H}F_2$	(e)	13.3	12.52	96–230	$CH_4/C_2H_4F_2/Br_2$ P	15
CH_3CF_3	(e)	22.2	13.18	243–379	$CF_3H/CH_3CF_3/Br_2$ P	15
CF_3CH_2F	(e)	18.2	12.73	130–322	$CH_2F_2/CF_3CH_2F/Br_2$ P	15
CF_2HCF_2H	(e)	18.1	12.75	118–283	$CH_2F_2/CF_3CH_2F/Br_2$ P	15
CF_3CF_2H	(e)	18.0	12.20	150–300	$CH_4/C_2F_5H/Br_2$	12
$CF_3CF_2CF_2H$		17.8	12.08	146–286	$CH_4/C_3F_7H/Br_2$ T	15
$CH_3CH_2CH_2C\mathbf{H}_2F$	(f)	11.6	13.2	62–185	$CH_3CH_2CH_2CH_2F/Br_2$ P	26
$CH_3CH_2C\mathbf{H}_2CH_2F$	(f)	11.5	13.1	62–185	$CH_3CH_2CH_2CH_2F/Br_2$ P	26
$CH_3C\mathbf{H}_2CH_2CH_2F$	(f)	(10.2)	(13.6)	62–185	$CH_3CH_2CH_2CH_2F/Br_2$ P	26
$C\mathbf{H}_3CH_2CH_2CH_2F$	(f)	13.0	13.0	62–185	$CH_3CH_2CH_2CH_2F/Br_2$ P	26
$CF_3CH_2C\mathbf{H}_2CH_2CH_3$	(g) (f)	11.0	13.2	0–230	$CF_3CH_2CH_2CH_2CH_3/Br_2$ P	26
$CF_3CH_2CH_2C\mathbf{H}_2CH_3$	(f)	(10.2)	(13.6)	0–230	$CF_3CH_2CH_2CH_2CH_3/Br_2$ P	26
$CF_3CH_2CH_2CH_2C\mathbf{H}_3$	(f)	13.0	13.1	0–230	$CF_3CH_2CH_2CH_2CH_3/Br_2$ P	26
Alcohols						
$C\mathbf{H}_3OH$		6.3	11.65	76–135	CH_3OH/Br_2 P	27
CH_3CH_2OH		2.6 ± 2.0		70–150	C_2H_5OH/Br_2 P	28

CHLORINE ATOM TRANSFER

Cl_2		6.9 ± 0.4	12.65 ± 0.2	20–60	Br_2/Cl_2 P	29

BROMINE ATOM TRANSFER

Alkyl halides						
CH_3Br		22.9	13.7	150–297	CH_4/Br_2 P, T	10, 17
CH_2Br_2			14.0			10, 17

Metathetical Reactions of Bromine Atoms—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
CCl_3Br		10.3	13.91	146–183	CCl_3Br/Br_2 T	30
Hydrogen halide						
HBr	(a)	43.8 41.7	14.4 13.9	700–1400 25–302	 H_2/Br_2 T	6 33, 17
Halogen						
BrCl		$k=(3.1\pm0.8)\times10^3$		20	Br_2/Cl_2 P	29

OXYGEN ATOM TRANSFER

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
N_2O		37	14.3	603–700	N_2O/Br_2 T	31

MISCELLANEOUS REACTIONS

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
$Br+Na_2=NaBr+Na$		$k=1.5\times10^{14}$		~300	Br$_2$/Na D.F.	35

Notes

(a) Estimated from a general review of kinetic data.

(b) Critical survey of literature data.

(c) These values are less reliable than those given for other compounds, by the same authors.

(d) All values are related to $Br+CH_3Br=CH_2Br+HBr$ as standard, for which $k=10^{13.73}\exp(-16050/RT)$.

(e) Measured relative to $CH_4+Br=CH_3+HBr$ for which $k=10^{13.15}\exp(-17300/RT)$. This is a recalculation of data from ref. 10. To compare these values with the others, E should be increased by 1 kcal/mole and log A by 0.65 units.

(f) The values at the δ or γ positions (bracketed) are assumed the same as for the 2 position in *n*-butane (ref. 11). The other values are calculated relative to this. These values must be considered very approximate.

(g) Very small quantities of $CF_3CHBrCH_2CH_2CH_3$ were formed, but not in sufficient quantities for the Arrhenius factors to be estimated.

(h) These values are believed to be in error (ref. 17)

(i) Measured relative to $Br+H_2=H+HBr$, for which $k=10^{14.43}\exp(-19{,}700/RT)$.

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Metathetical Reactions of Iodine Atoms

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		HYDROGEN ATOM TRANSFER				
Hydrogen		*(kcal mole^{-1})*	*(cm^3 mole^{-1} sec^{-1})*	°C		
H_2		33.9 ± 0.3	14.32 ± 0.11	105–360	H_2/I_2 T	1
		33.5 ± 0.2	14.20 ± 0.07	394–527	H_2/I_2 T	2
		$k = 4.6 \times 10^6$		700	HI and H_2/I_2 T	3, 4
D_2		34.5 ± 0.3	14.06 ± 0.10	394–527	D_2/I_2 T	5
Alkanes						
CH_4	(a)	33.5	14.70	260–316		6, 7
		34.1	14.70	260–316	CH_4/I_2 T	7
		35.0 ± 1.1	14.95	275–345	CH_4/I_2 T	8
C_2H_6		27.9	14.22	263–303	C_2H_5I/HI T	9
C_3H_8		25.5 ± 1	14.53 ± 0.36	307–340	C_3H_8/I_2 T	10
$CH_3C\mathbf{H}_2CH_3$		25.0	14.22	307–340	C_3H_8/I_2 T	10
i-C_4H_{10}		21.4 ± 0.5	13.88 ± 0.15	252–310	i-C_4H_{10}/I_2 T	11
Alkenes						
$CH_2{:}CHC\mathbf{H}_3$		18.04 ± 0.32	13.25 ± 0.14	208–300	$CH_2{:}CHCH_3/I_2$ T	22
1-$CH_2{:}CHCH_2CH_3$		13.2 ± 0.4	12.83 ± 0.15	204–253	$CH_2{:}CHCH_2CH_3/I_2$ T	12
Aromatic hydrocarbon						
$C_6H_5CH_3$		$k = 4.8 \times 10^7$		501	$C_2H_5I/C_6H_5CH_3$ T	13
Aldehyde						
CH_3CHO		15.7	13.3	222–268	CH_3COI/HI T	14
Alcohol						
$(CH_3)_2C\mathbf{H}OH$		20.5	14.07	207–300	$(CH_3)_2CHOH/I_2$ T	23
		IODINE ATOM TRANSFER				
Alkyl halides						
CH_3I		19.8	14.3	270–320	CH_3I/HI T	15, 16
		$\geqslant 20.5$	($k = 1.60 \times 10^3$)	280	CH_3I/HI T	17, 16
		20.5 ± 0.5	14.4 ± 0.2	260–316	CH_3I/HI T	6
		19.2	13.71		CH_3I/HI T	18
CF_3I		17.60	13.8	167–485	CF_3I/HI T	18
C_2H_5I		16.7	13.62	250–300	C_2H_5I/HI T	15, 16
		$\geqslant 18.2$	($k = 6.8 \times 10^3$)	260	C_2H_5I/HI T	17, 16
		17.1 ± 0.7	14.01 ± 0.28	263–303	C_2H_5I/HI T	9
n-C_3H_7I		$\geqslant 18.5$	($k = 12.9 \times 10^3$)	290	n-C_3H_7I/HI T	17, 16
$ICH_2CH_2CH_2I$		19.5	14.0			19
$(CH_3)_3CI$		13.0 ± 0.7	13.7 ± 0.4	252–310	$(CH_3)_3CH/I_2$ T	11

Reactions of Sodium Atoms

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Metathetical Reactions of Sodium Atoms

Reactants	Notes	(a)E	$\log_{10} k$	Temperature range	Radical source	References
			FLUORINE ATOM TRANSFER			
Halogenated alkanes		*(kcal mole^{-1})*	*(cm^3 mole^{-1} sec^{-1})*	°C		
CF_2	(b) (e)		6.5 log $(k_f)^{1/2}$	313	D.F.	4
	(e)		5.0 log $(k_f)^{1/2}$	310	D.F.	5
CFH_2	(b) (c)		6.1 log $(k_e)^{1/2}$	313	D.F.	4
CF_2H	(b) (d)		6.2 log $(k_e)^{1/2}$	313	D.F.	4
CF_3	(b)		13.83	313	D.F.	4
			13.97	310	D.F.	5
CFH_3		> 25	< 8.7	240	D.F.	1, 6
		~ 18.5	7.3	247		2, 3
CH_2F_2		14.0	8.8	247		2, 3
CHF_3		14.0	8.8	247		2, 3
CF_4		12.6	9.4	247		2, 3
cyclo-C_6F_{12}		7.1	11.7	247		2, 3
cyclo-$C_6F_{11}CF_3$		6.7	12.0	247		2, 3
Alkenes						
C_2F_4		8.8	11.0	247		2, 3
Acids and acid halides						
CF_3COOH		4.0	13.0	247		2, 3
CF_3COF		7.6	11.5	247		2, 3
Halogenated aromatics						
C_6H_5F			< 8.7	247		19
Miscellaneous						
SF_6		3.3	13.3	247		2, 3
			CHLORINE ATOM TRANSFER			
Halogenated alkanes						
CH_3Cl		7.5	10.7	240	D.F.	1, 6
			10.9	270		7
			11.8	325	M.D.F.	8
	(f)	9.8	11.1	313	D.F.	9
		8.2			D.F.	10
			11.8	220	M.L.	11

Metathetical Reactions of Sodium Atoms—Continued

Reactants	Notes	(a) E	$\log_{10} k$	Temperature range	Radical source	References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
CH_2Cl_2			11.75	275	D.F.	1, 6
			12.4	270		7
			11.8	250	D.F.	12
$CHCl_3$			12.7	275	D.F.	1, 6
			13.5	270		7
			13.0	250	D.F.	12
CCl_4			13.3	275	D.F.	1, 6
			14.5	270		7
			14.0	250	D.F.	12
	(g) (f)	8.4	12.17	310	M.D.F.	13
			14.35	247	D.F.	14
CH_2FCl	(g) (f)	10.1	10.97	313	D.F.	9
CHF_2Cl			10.0	247		3
	(g) (f)	10.0	11.0	313	D.F.	9
CF_3Cl			10.7	247		3
		9.2	11.3	313	D.F.	9
	(f)	7.4		275–315	D.F.	15
	(g) (f)	10.2	10.9	310	M.D.F.	13
CF_2Cl_2	(g) (f)	9.0 to 9.5	11.5 to 11.7	310	M.D.F.	13
$CFCl_3$	(g) (f)	8.7 to 9.2	11.8 to 11.9	310	M.D.F.	13
C_2H_5Cl			10.9	275	D.F.	6, 1
		10.2		260–380	D.F.	16, 17
		7.8		292–391	D.F.	10
CH_2ClCH_2Cl			11.8	275	D.F.	6
	(a)	7.0	12.0	285	D.F.	18
CH_3CHCl_2			11.9	275	D.F.	6
CH_3CCl_3			13.6	247	D.F.	14
$CH_3CH_2CH_2Cl$	(a)	9.1	11.1	275	D.F.	6
	(a)	9.0	11.0	261	D.F.	18
			10.7	267	D.F.	19
$CH_3CHClCH_3$			11.2	275	D.F.	6
$CH_2ClCH_2CH_2Cl$			11.7	275	D.F.	6
$CH_3CHClCH_2Cl$			12.0	275	D.F.	6
$CH_3CH_2CHCl_2$			12.2	275	D.F.	6
$(CH_3)_2CCl_2$			12.4	275	D.F.	6
			12.6	247	D.F.	14
$CH_3CH_2CH_2CH_2Cl$			11.2	275	D.F.	6
$CH_3CH_2CHClCH_3$			11.4	275	D.F.	6

Metathetical Reactions of Sodium Atoms—Continued

Reactants	Notes	(a) *E*	$\log_{10} k$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$(CH_3)_2CHCH_2Cl$			11.2	275	D.F.	6
$(CH_3)_3CCl$			11.5	275	D.F.	6
			11.4	247	D.F.	14
$CH_3CH_2CH_2CH_2CH_2Cl$			11.4	275	D.F.	6
$(CH_3)_2CHCH_2CH_2Cl$			11.4	275	D.F.	6
$(CH_3)_2CClCH_2CH_3$			11.9	275	D.F.	6
Alkenes						
$CH_2{:}CHCl$			10.7	275	D.F.	6
trans-CHCl:CHCl			11.3	275	D.F.	6
cis-CHCl:CHCl			11.4	275	D.F.	6
$CH_2{:}CHCH_2Cl$			12.3	275	D.F.	6
			12.5	260	D.F.	18
$CH_2{:}CClCH_3$			11.0	275	D.F.	6
$C_6H_5CH{:}CHCl$			13.0	275	D.F.	18
$C_6H_5CH{:}CHCH_2Cl$			13.9	275	D.F.	18
Aromatic chlorides and their derivatives						
C_6H_5Cl			9.4	247	D.F.	19
			11.2	244	M.L.	25
			11.8	270	D.F.	1
$C_6H_5CH_2Cl$			14.7	275	D.F.	6
			13.7	284	D.F.	18
$C_6H_5CH_2CH_2Cl$			13.4	285	D.F.	18
o-FC_6H_4Cl			10.3	247	D.F.	19
m-FC_6H_4Cl			9.8	247	D.F.	19
p-FC_6H_4Cl			9.1	247	D.F.	19
o-ClC_6H_4Cl			11.2	247	D.F.	19
o-$CH_3OOCC_6H_4Cl$			13.4	247	D.F.	19
2:Cl-pyridine			12.7	247	D.F.	19
3:Cl-pyridine			10.0	247	D.F.	19
Cyanides						
$CNCH_2Cl$			13.9	285	D.F.	18

Metathetical Reactions of Sodium Atoms—Continued

Reactants	Notes	(a) E	$\log_{10} k$	Temperature range	Radical source	References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°*C*		
$CNCH_2CH_2Cl$			11.8	285	D.F.	18
Acids, acid chlorides, esters, etc.						
$CH_2ClCOOH$			13.3	247		3
CH_3COCl			12.7	275	D.F.	6, 1
			13.4	247	D.F.	3, 2
		0			D.F.	10
C_6H_5COCl			14.7	240	D.F.	1
$ClCOOC_2H_5$			11.6	247	D.F.	3, 2
$CH_2ClCOOC_2H_5$			13.2	247	D.F.	3, 2
$ClCH_2CH_2OH$			11.7	285	D.F.	18
CH_3COCH_2Cl			13.7	275	D.F.	6
			14.0	247	D.F.	2
CH_3OCH_2Cl			11.3	247		3, 2
Polyhalides						
BCl_3			11.7	270	D.F.	7
$SiCl_4$			11.6	270	D.F.	7
			11.8	247	D.F.	14
CH_3SiCl_3			9.8	247	D.F.	14
$(CH_3)_2SiCl_2$			9.3	247	D.F.	14
$(CH_3)_3SiCl$			9.4	247	D.F.	14
PCl_3			14.2	270	D.F.	7
$TiCl_4$			14.0	270	D.F.	7
$GeCl_4$			14.7	270	D.F.	7
$AsCl_3$			14.2	270	D.F.	7
$SnCl_4$			14.5	270	D.F.	7
SCl_2			14.8	270	D.F.	7
S_2Cl_2			14.2	270	D.F.	7
Oxychlorides						
$COCl_2$			13.9	270	D.F.	7
CrO_2Cl_2			14.1	270	D.F.	7
$POCl_3$			14.4	270	D.F.	7

Metathetical Reactions of Sodium Atoms—Continued

Reactants	Notes	$^{(a)}E$	$\log_{10} k$	Temperature range	Radical source	References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
Halogens and pseudohalogens						
Cl_2			14.6		Dil. F.	20
CNCl			14.0	285	D.F.	18
			13.9	250	D.F.	1
Hydrogen halide						
HCl			12.4	327	Dil. F.	21, 20
BROMINE ATOM TRANSFER						
Ialogenated alkanes						
CH_3Br			13.3	240	D.F.	1, 6
			12.8	270		7
			12.6	255	D.F.	12
			12.2	200	M.L.	11
			12.8	242	M.L.	11
	(h)	3.4				10
CH_2Br_2			13.6	255	D.F.	12
			13.5	255	M.L.	12
$CHBr_3$			14.6	255	D.F.	12
			13.9	255	M.L.	12
$CFBr_3$			14.3	255	D.F.	12
CF_3Br	(a)	2.3		285	D.F.	15
$CHFBr_2$			13.7	255	M.L.	12
CH_2ClBr			13.3	255	D.F.	12
			13.3	255	M.L.	12
$CHClBr_2$			14.3	255	D.F.	12
			13.7	255	M.L.	12
$CHCl_2Br$			14.0	255	D.F.	12
			13.6	255	M.L.	12
CCl_3Br			14.5	255	D.F.	12
			14.0	255	M.L.	12
C_2H_5Br			12.8	240	D.F.	1
			12.4	247	D.F.	19
			12.7	263	D.F.	18

Metathetical Reactions of Sodium Atoms—Continued

Reactants	Notes	(a) E	$\log_{10} k$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
CH_2BrCH_2Br			13.3	247		3
cyclo-C_3H_5Br			12.0	247	D.F.	22
cyclo-C_4H_7Br			12.6	247	D.F.	22
cyclo-C_5H_9Br			13.1	247	D.F.	22
$CH_3CH_2CH_2CH_2CH_2Br$			12.8	247	D.F.	22
cyclo-$C_6H_{11}Br$			12.7			23
			12.7	247	D.F.	22
Alkenes						
$CH_2{:}CHBr$			12.4	269	D.F.	18
			11.2	247	D.F.	22
$C_6H_5CH{:}CHBr$			13.1	270	D.F.	18
$C_6H_5CH{:}CHCH_2Br$			14.6	285	D.F.	18
Aromatic bromides and their derivatives						
C_6H_5Br			12.3	255	M.L.	24
			11.4	247	D.F.	19
			13.2	244	M.L.	25
			13.4	260	D.F.	1
			12.1	247	D.F.	14
o-ClC_6H_4Br			12.6	247	D.F.	19
m-ClC_6H_4Br			11.9	247	D.F.	19
p-ClC_6H_4Br			11.6	247	D.F.	19
o-BrC_6H_4Br			13.4	247	D.F.	19
o-CNC_6H_4Br			13.3	247	D.F.	19
m-CNC_6H_4Br			12.6	247	D.F.	19
p-CNC_6H_4Br			12.8	247	D.F.	19
o-HOC_6H_4Br			12.2	247	D.F.	19
m-HOC_6H_4Br			11.8	247	D.F.	19
o-$CH_3C_6H_4Br$			11.5	247	D.F.	19
m-$CH_3C_6H_4Br$			11.2	247	D.F.	19

Metathetical Reactions of Sodium Atoms – Continued

Reactants	Notes	(a) E	$\log_{10} k$	Temperature range	Radical source	References
		(kcal $mole^{-1}$)	(cm^3 $mole^{-1}$ sec^{-1})	°C		
p-$CH_3C_6H_4Br$			11.3	247	D.F.	19
o-$CH_3OC_6H_4Br$			11.9	247	D.F.	19
p-$CH_3OC_6H_4Br$			11.6	247	D.F.	19
o-$CH_3OOC_6H_4Br$			13.8	247	D.F.	19
m-$CH_3OOC_6H_4Br$			12.6	247	D.F.	19
p-$CH_3OOC_6H_4Br$			12.6	247	D.F.	19
α-Bromonaphthalene			12.7	247		3
β-Bromonaphthalene			12.1	247		3
2:Br-pyridine			13.3	247	D.F.	19
3:Br-pyridine			11.9	247	D.F.	19
$C_6H_5CH_2CH_2Br$			13.6	280	D.F.	18
Acid bromide						
CH_3COBr			13.9	300	D.F.	1
Halogens and pseudo-halogens						
CNBr			14.1	273	D.F.	18
Hydrogen halide						
HBr			13.8	327	Dil. F.	21, 20

IODINE ATOM TRANSFER

Halogenated alkanes						
CH_3I			14.7	240	D.F.	6
			14.5	240	M.L.	11
			13.7	250	M.L.	12
			13.6	255	D.F.	12
			13.6	277	D.F.	23
		0			D.F.	10
CF_3I			14.0	247		3
		1.7		285–295	D.F.	15
C_2H_5I			14.0	240–270	D.F.	1
			14.3	276	D.F.	18
$CH_3CH_2CH_2I$			13.4	240	D.F.	1

Metathetical Reactions of Sodium Atoms—Continued

Reactants	Notes	(a) E	$\log_{10} k$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
Alkenes						
CH_2:CHI			13.4	263	D.F.	18
Aromatic iodides						
C_6H_5I			14.7 14.3	240 244	D.F. M.L.	1 25
Halogens						
I_2			14.8		Dil. F.	20
Hydrogen halide						
HI			14.7	327	Dil. F.	20, 21
CYANIDE GROUP TRANSFER						
CH_3CN			<6.6	247		3
$C_6H_5CH_2CN$			9.8	247		3
$CH_2(CN)COOC_2H_5$			11.6	247		3

Notes

(a) The activation energies E are calculated from the formula $k=10^{14.7}\exp(-E/RT)$.

(b) These values are lower limits.

(c) k_e is the rate contant for the combination reaction $2CFH_2=C_2F_2H_4$.

(d) k_c is the rate constant for the combination reaction $2CF_2H=C_2F_4H_2$.

(e) k_f is the rate constant for the combination reaction $2CF_2=C_2F_4$.

(f) Calculated assuming a steric factor of unity.

(g) These values refer to the rate constants for the primary process.

(h) Estimated from a critical survey of literature data.

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Metathetical Reactions of Potassium Atoms

Reactants	Notes	E	$\log_{10} k$	Temperature range	Radical source	Reference
CHLORINE ATOM TRANSFER						
(*kcal mole*)$^{-1}$			($cm^3\ mole^{-1}\ sec^{-1}$)	°*C*		
HCl			14.0	327	Dil F.	1, 2
Cl_2	(b)					
BROMINE ATOM TRANSFER						
HBr			14.6	327	Dil F.	1, 2
	(a)	3.4			M.B.	3
Br_2	(b)					
IODINE ATOM TRANSFER						
HI			15.3	327	Dil F.	1, 2
CH_3I	(a)	< 0.3			M.B.	5

Notes

(a) These quantities cannot be identified with normal Arrhenius factors.

(b) See reference 4.

Ratios of Rate Constants (Potassium Atoms)

The table refers to ratios of rate constants for reactions of the following types:

$$K + R_1X = KX + R_1 \qquad (1)$$

$$K + R_2X = KX + R_2 \qquad (2)$$

where X is any halogen atom.

R_1X	R_2X	Notes	$E_1 - E_2$	A_2/A_1	k_2/k_1	Temperature range	Radical source	Reference
			(*kcal mole*$^{-1}$)			°*C*		
CH_3Cl	C_2H_5Cl		0.4 ± 0.09	0.83 ± 0.10		217–333	D.F.	6
CH_3Cl	CH_3COCl				360	285	D.F.	6
C_2H_5Cl	$(CH_3)_2CHCl$		−0.13 ± 0.14	2.18 ± 0.25		238–325	D.F.	7
C_2H_5Cl	$(CH_3)_3CCl$		2.27 ± 0.55	0.78 ± 0.4		229–275	D.F.	7
CH_3Br	C_2H_5Cl		4.4	0.52		230–316	D.F.	6
CH_3Br	CH_3COCl		1.4	3.5		229–318	D.F.	6
CH_3I	C_2H_5Cl				38	285	D.F.	6
CH_3I	CH_3COCl		0	7.0		238–322	D.F.	6

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Metathetical Reactions of Methyne Radicals

Reaction	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
$CH+NH_3=HCN+H_2+H$		$k>6\times10^{10}$		no indication	C_2H_2/NH_3 flames	1

Reference

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Ratios of Rate Constants (Methylene Radicals)

Reactions	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source		Reference
		(*kcal mole*$^{-1}$)			°C			
(1) $CH_2 + CH_2CO = C_2H_4 + CO$	(a)			2.3	6–9			1
(2) $CH_2 + CO = CH_2CO$	(b)			1.25	4–16	$CH_2CO/^{13}CO$	P	1
(1) $CH_2 + CH_2CO = C_2H_4 + CO$								
(2) $CH_2 + C_2H_4 = C_3H_6$		4.8			28–81	CH_2CO/O_2	P	2
(1) $CH_2 + CH_2CO = C_2H_4 + CO$								
(2) $CH_2 + C_2H_2 = C_3H_4$	(c)			0.9 ± 0.1	no indication	CH_2CO/C_2H_2	F.P.	3
(1) $CH_2 + CH_2CO = C_2H_4 + CO$								
(2) $CH_2 + H_2 = CH_3 + H$		-0.8			-40–99	CH_2CO/H_2	P	4, 5, 7
(1) $CH_2 + CH_2CO = C_2H_4 + CO$								
(2) $CH_2 + CD_4 = CH_2D_2 + CD_2$		-0.9	0.15		27–298	CH_2CO/CD_4	P	6, 7

Notes

(a) and (b) represent two methods of estimating k_1/k_2: the discrepancy lies outside the experimental error.

(c) k_2 represents the sum of the rate constants for the reactions $CH_2 + C_2H_2 = HC{:}CCH_3$ and $CH_2 + C_2H_2 = H_2C{:}C{:}CH_2$.

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Methyl Radical Reactions

Index

(a) Hydrogen atom transfer

Reaction with

(h) Ratios of rate constants

Metathetical Reactions of Methyl Radicals

HYDROGEN ATOM TRANSFER

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
Hydrogen		(*kcal mole^{-1}*)	(*cm^3 mole^{-1} sec^{-1}*)	°C		
H_2	(d)	10.0 ± 0.5	11.5	130–290	CH_3COCH_3 P	1, 2, 3
		9.9 ± 0.5	11.7	25–250	$Hg(CH_3)_2$ T	4, 3
		13 ± 2	13.4	50–250	$Cd(CH_3)_2$ P	5
	(a)	13.2 ± 1.0	12.5	136–318	CH_3COCH_3 P	6
		10.2 ± 0.5	11.52	99–207	CH_2CO P	7
	(b)	12.85	12.75			8
		$k = 4.1 \times 10^8$		507	CH_3OCH_3 T	9
		10.2	12.50	697–863	H_2/O_2 ignition	10
	(y)	10.2 ± 0.2	11.7	130–290	CD_3COCD_3 P	1, 2
	(y)	11.1	12.0	150–300	CD_3COCD_3 P	3
		10.0	11.5			
$\mathbf{H}D$		10.0	11.1	140–296	CH_3COCH_3 P	3
	(y)	10.7	11.4	137–298	CD_3COCD_3 P	3
$H\mathbf{D}$		11.5	11.5	135–296	CH_3COCH_3 P	3
	(y)	10.7	11.2	137–299	CD_3COCD_3 P	3
D_2	(d)	11.8 ± 0.1	11.8	130–290	CH_3COCH_3 P	1, 2, 3
	(c)	15.3 ± 1.0	14.8	258–451	CH_3CHO P	6
	(a)	14.3 ± 0.6	12.5	150–458	CH_3COCH_3 P	6
		12.7 ± 0.3	12.3	27–253	$Hg(CH_3)_2$ P	12
		$k = 2.0 \times 10^8$		507	CH_3OCH_3 T	9
		12.1 ± 0.6	11.79	151–299	CH_3COCH_3 P	13
		11.9	11.4	140–425	CH_3COCH_3 P	14
	(y)	10.9 ± 0.3	11.4	130–290	CD_3COCD_3 P	1, 2
Alkanes						
CH_4		14.9	12.00	200–350	CH_3COCH_3 P	16, 17
	(y)	$k = 1.7 \times 10^5$		182	CD_3COCD_3 P	18, 19
	(y)	14.3	11.5	350–525	CD_3COCD_3 P, T	20
	(y)	$k = 3.6 \times 10^6$		320	CD_3COCD_3 P	21
	(y)	14.1	11.8	200–350		17
$CH_3\mathbf{D}$	(y) (e)	12.8	10.42	27–327		22
$CD_3\mathbf{H}$	(e)	13.8	11.21	27–327		22
CD_4		12.93 ± 0.65	11.26	153–428	CH_3COCH_3 P	23, 17
	(y)	18.4	12.95	200–350	CD_3COCD_3 P	17
C_2H_6		12.0	10.6	770–890	C_2H_6 T	24
		$k = 1.4 \times 10^8$		630	C_2H_6 T	25
	(y) (f)	9.9 ± 1.1		500–560	CD_3CDO T	29, 51
	(y)	10.4 ± 0.4	11.3	116–294	CD_3COCD_3 P	19, 26
	(y)	11.8	12.21	162–341	CD_3COCD_3 P	21
	(y)	12.1	12.3	260–490	CD_3COCD_3 P	27
	(y)	11.5 ± 0.2	11.9	246–524	CD_3COCD_3 P, T	28
$C\mathbf{H}_3CD_3$	(y)	12.2	12.0	260–490	CD_3COCD_3 P	27, 39
$CH_3C\mathbf{D}_3$	(y)	14.1	12.1	260–490	CD_3COCD_3 P	27, 39

Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
$\mathbf{C_2D_6}$		14.8 ± 0.3	12.3	328–507	CH_3COCH_3 P, T	28
	(y)	13.6	12.3	260–490	CD_3COCD_3 P	27
C_3H_8	(g)	$k=3.3\times10^9$		580	C_3H_8 T	29
		10.3	11.91	300–460	CD_3COCD_3 P	30
$C\mathbf{H}_3CD_2C\mathbf{H}_3$	(y)	11.6	12.08	300–450	CD_3COCD_3 P	31, 39
$CH_3C\mathbf{D}_2CH_3$	(y)	11.6	11.85	300–450	CD_3COCD_3 P	31, 39
n-C_4H_{10}		8.3 ± 0.2	11.0	122–198	CH_3COCH_3 P	19, 26
		8.2 ± 0.5	11.3	130–220	$Hg(CH_3)_2$ P	32
	(h)	9.5 ± 0.5	11.5		$Hg(CH_3)_2$ P	32
		8.6 ± 0.3	11.2	92–223	$Hg(CH_3)_2$ P	33
	(h)	$k=1.3\times10^7$		182	$Hg(CH_3)_2$ P	34
		9.1 ± 0.3	11.4	79–162	$(CH_3)_2N_2$ P	35
		9.6	11.92	250–449	CD_3COCD_3 P	36
	(y) (f)	10.3 ± 0.2		500–560	CD_3CDO T	29
$C\mathbf{H}_3CD_2CD_2C\mathbf{H}_3$	(y)	11.7	12.09	356–450	CD_3COCD_3 P	36
$CH_3C\mathbf{D}_2C\mathbf{D}_2CH_3$	(y)	11.7	12.12	356–450	CD_3COCD_3 P	36
iso-C_4H_{10}		7.6 ± 0.2	11.0	76–194	CH_3COCH_3 P	19, 26
		7.4 ± 0.3	10.8	93–220	$Hg(CH_3)_2$ P	33
		6.6 ± 0.3	10.3	25–169	$(CH_3)_2N_2$ P	35
		7.7	10.3	111–146	D.T.B.P. T	37
	(y)	$k=2.05\times10^7$		198	CD_3COCD_3 P	38
	(y) (f)	9.0 ± 0.6		500–560	CD_3CDO T	29
$(CH_3)_3C\mathbf{H}$	(y)	8.2	11.47	300–460	CD_3COCD_3 P	30
$(C\mathbf{H}_3)_3CD$	(y)	11.7	12.26	300–460	CD_3COCD_3 P	30, 39
$(CH_3)_3C\mathbf{D}$	(y)	9.8	11.57	300–460	CD_3COCD_3 P	30, 39
n-C_5H_{12}		8.1 ± 0.2	11.0	89–178	CH_3COCH_3 P	19, 26
		$k=1.0\times10^9$		540	n-C_5H_{12} T	40
		9.9 ± 2.7		540–580	n-C_5H_{12} T	29
iso-C_5H_{12}		$k=0.9\times10^9$		540	iso-C_5H_{12} T	40
neo-C_5H_{12}		10.0 ± 0.3	11.3	138–292	CH_3COCH_3 P	19, 26
		10.4 ± 0.3	11.3	131–251	$Hg(CH_3)_2$ P	33
		$k=0.2\times10^9$		540	neo-C_5H_{12} T	40
	(y) (f)	10.8 ± 0.2		500–560	CD_3CDO T	29
n-C_6H_{14}		8.1 ± 0.2	11.1	92–184	CH_3COCH_3 P	19, 26
$(CH_3)_2CHCH(CH_3)_2$		6.9 ± 0.2	10.8	27–190	CH_3COCH_3 P	19, 26
		6.8 ± 0.2	10.7	28–220	$Hg(CH_3)_2$ P	33
	(y) (f)	7.3 ± 0.8		500–560	CD_3CDO T	29
	(y)	7.8 ± 0.4	11.3	166–293	CD_3COCD_3 P	26
$(C_2H_5)_3CH$		6.8 ± 0.3	10.5	76–238	$Hg(CH_3)_2$ P	41
n-C_8H_{18}		$k=1.6\times10^9$		500	n-C_8H_{18} T	40

Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(kcal mole⁻¹)	*(cm³ mole⁻¹ sec⁻¹)*	°C		
$(CH_3)_3CCH_2CH(CH_3)_2$		$k=0.7\times10^9$		500	$(CH_3)_3CCH_2CH(CH_3)_2$ T	40
$(CH_3)_2CHCH(CH_3)CH(CH_3)_2$		$k=1.9\times10^9$		500	$(CH_3)_2CHCH(CH_3)CH(CH_3)_2$ T	40
	(y)	7.9 ± 0.4	11.3	141–332	CD_3COCD_3 P	26
$(CH_3)_3CC(CH_3)_3$	(y)	9.5 ± 0.4	11.3	162–322	CD_3COCD_3 P	26
Cyclo-alkanes						
cyclo-C_3H_6		10.2 ± 1.0	11.1	100–250	$Hg(CH_3)_2$ P	42
	(y)	10.3 ± 0.4	11.0	139–292	CD_3COCD_3 P	43
	(y)	12.9	12.18	248–404	CD_3COCD_3 P	44
cyclo-C_4H_8	(y)	9.3 ± 0.4	11.4	154–307	CD_3COCD_3 P	43
		10.1	12.18	262–402	CD_3COCD_3 P	45
cyclo-C_5H_{10}	(i)	$k=5.7\times10^7$		303	$Hg(CH_3)_2$ T	46
	(y)	8.3 ± 0.2	11.4	66–296	CD_3COCD_3 P	43
	(y)	9.1	12.24	250–402	CD_3COCD_3 P	44
	(y)	9.0	12.10	160–500	CD_3COCD_3 P	47
cyclo-C_6H_{12}		8.3 ± 0.2	11.3	65–189	CH_3COCH_3 P	43
		8.3 ± 0.3	11.2	81–220	$Hg(CH_3)_2$ P	33
	(y)	9.5	12.47	254–481	CD_3COCD_3 P	48
cyclo-C_7H_{14}	(y)	8.9	12.49			48
Alkenes						
$CH_2{:}CH_2$	(y)	10.0 ± 0.4	11.3	188–340	CD_3COCD_3 P	49
	(y) (f)	7.3 ± 1.0		500–560	CD_3CDO T	29
$CH_3CH{:}CH_2$		8.2	11.04	107–168	D.T.B.P	50
	(y)	7.7 ± 0.4	10.8	163–304	CD_3COCD_3 P	49
	(y) (f)	8.0 ± 0.3		500–560	CD_3CDO T	29, 51
$CH_3CH{:}CHCH_3$	(y)	7.7 ± 0.4	11.1	188–342	CD_3COCD_3 P	49
$CH_2{:}CHCH_2CH_3$	(y)	7.6 ± 0.4	11.2	189–340	CD_3COCD_3 P	49
$(CH_3)_2C{:}CH_2$	(y)	7.3 ± 0.4	10.9	168–304	CD_3COCD_3 P	49
$CH_3CH_2CH_2CH{:}CH_2$	(y)	7.6 ± 0.4	11.2	188–346	CD_3COCD_3 P	49
$(CH_3)_2CHCH{:}CH_2$	(y)	7.4 ± 0.4	11.3	189–346	CD_3COCD_3 P	49
$(CH_3)_2C{:}C(CH_3)_2$	(y)	7.8 ± 0.4	11.6	188–341	CD_3COCD_3 P	49
Alkynes						
$HC{:}CH$	(y)	14.0		200–500	CD_3COCD_3 P	52
$DC{:}CD$		18.4		200–500	CH_3COCH_3 P	52

Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(kcal mole⁻¹)	*(cm³ mole⁻¹ sec⁻¹)*	*°C*		
$CH_3C{:}CCH_3$	(y)	8.6 ± 0.4	11.6	213–346	CD_3COCD_3 P	43
$CH{:}CCH_2CH_3$	(y)	9.1 ± 0.4	11.9	183–347	CD_3COCD_3 P	43
Aromatic hydrocarbons						
C_6H_6		$k = 4.48 \times 10^6$		209	D.T.B.P. T	53
	(y)	9.2 ± 0.4	10.4	183–327	CD_3COCD_3 P	43
$C_6H_5CH_3$	(h)	7 ± 2	10.0	103–249	$Hg(CH_3)_2$ P	54
		11.0 ± 2		130–230	D.T.B.P. P	55
		7.3 ± 0.3	11.2	149–250	$Hg(CH_3)_2$ P	33
	(j)	13.03 ± 0.27	12.92 ± 0.08	346–701		56, 57, 58
	(z)	7.4 ± 0.3	10.47	100–253	CH_3COCH_3 P	59
		9.2 ± 0.3	11.4	159–270	D.T.B.P. T	53
		$k = (4.0 \pm 0.8) \times 10^5$		60	$CH_3N_2CH_3$ P	60
	(y)	8.3 ± 0.3	11.0	120–334	CD_3COCD_3 P	43
$C_6\mathbf{H}_5CD_3$		$k = (2.3 \pm 0.4) \times 10^4$		60	$CH_3N_2CH_3$ P	60
		10.2	10.7	100–300		72
$C_6H_5\mathbf{CD_3}$		$k = (2.6 \pm 0.2) \times 10^4$		60	$CH_3N_2CH_3$ P	60
		11.3	11.8	102–284	CH_3COCH_3 P	72
$C_6D_5\mathbf{CH_3}$		$k = (3.8 \pm 0.8) \times 10^5$		60	$CH_3N_2CH_3$ P	60
		9.6	11.6	106–284	CH_3COCH_3 P	72
$C_6\mathbf{D}_5CH_3$		$k = (1.0 \pm 0.2) \times 10^4$		60	$CH_3N_2CH_3$ P	60
		$k = 5.1 \times 10^4$		182	CH_3COCH_3 P	72
$C_6D_5CD_3$		$k = (3.7 \pm 0.2) \times 10^4$		60	$CH_3N_2CH_3$ P	60
$C_6H_5C_2H_5$	(z)	7.0 ± 0.3	10.82	85–183	CH_3COCH_3 P	59
$C_6H_5CH(CH_3)_2$	(z)	6.4 ± 0.5	10.76	123–249	CH_3COCH_3 P	59
o-$C_6H_4(CH_3)_2$	(z)	7.8 ± 0.3	11.13	101–205	CH_3COCH_3 P	61
m-$C_6H_4(CH_3)_2$	(z)	8.5 ± 0.3	11.45	100–197	CH_3COCH_3 P	61
p-$C_6H_4(CH_3)_2$	(z)	7.4 ± 0.2	10.82	99–197	CH_3COCH_3 P	61
	(k)	$k = 3.1 \times 10^7$		484	*p*-$C_6H_4(CH_3)_2$ T	62
$C_6H_4(CH_3)_2$	(k) (l)	$k = 6.9 \times 10^9$		700	$C_6H_4(CH_3)_2$ T	63
Halogenated aromatics						
o-$CH_3C_6H_4F$	(z)	6.0 ± 0.4	9.76	330–460	CH_3COCH_3 P	64
m-$CH_3C_6H_4F$	(z)	7.1 ± 0.2	10.32	330–460	CH_3COCH_3 P	64
p-$CH_3C_6H_4F$	(z)	5.7 ± 0.4	9.60	330–460	CH_3COCH_3 P	64

Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
Alcohols						
CH_3OH		8.2 ± 0.2	10.7	103–219	CH_3COCH_3 P	43
		8.2 ± 0.5	10.6	100–250	$Hg(CH_3)_2$ P	42
		8.7 ± 0.2	10.76 ± 0.07	133–199	CH_3COCH_3 P	65
	(y)	8.4 ± 0.1	10.68 ± 0.05	125–250	CD_3COCD_3 P	73
$C\mathbf{H}_3OH$	(m)	10.4	11.38	133–199	CH_3COCH_3 P	65
	(y) (m)	8.1	10.38	125–250	CD_3COCD_3 P	73
$CD_3O\mathbf{H}$		6.4 ± 0.7	9.25 ± 0.3	133–199	CH_3COCH_3 P	65
	(y)	9.0 ± 0.1	10.46 ± 0.03	125–245	CD_3COCD_3 P	73
$C\mathbf{D}_3OH$		11.7 ± 0.6	11.25 ± 0.28	133–199	CH_3COCH_3 P	65
	(y)	9.3 ± 0.1	10.18 ± 0.06	125–245	CD_3COCD_3 P	73
C_2H_5OH	(y)	8.7 ± 0.4	11.5	189–341	CD_3COCD_3 P	43
$(CH_3)_2CH(OH)$	(y)	7.3 ± 0.4	11.0	214–347	CD_3COCD_3 P	43
Thiols						
CH_3SH		$k = 1.8 \times 10^7$		30	CH_3COCH_3 P	66
$CD_3S\mathbf{H}$		4.1 ± 0.2	11.03 ± 0.15	130–200	CH_3COCH_3 P	74
$C\mathbf{D}_3SH$		8.3 ± 0.1	10.88 ± 0.05	130–200	CH_3COCH_3 P	74
C_2H_5SH		$k = 3.5 \times 10^7$		30	CH_3COCH_3 P	66
$(CH_3)_2CHSH$		$k = 4.1 \times 10^7$		30	CH_3COCH_3 P	66
$(CH_3)_3CSH$		$k = 5.9 \times 10^7$		30	CH_3COCH_3 P	66
Amines (primary)						
CH_3NH_2		7.6	10.9	125–157	D.T.B.P. T	67
		7.2 ± 0.2	10.59 ± 0.12		$CH_3N_2CH_3$ P	68
	(y)	8.4 ± 0.4	11.3	183–340	CD_3COCD_3 P	43
$C\mathbf{H}_3NH_2$	(m)	8.7 ± 0.7	10.99 ± 0.37	120–175	$CH_3N_2CH_3$ P	69, 68
$CH_3N\mathbf{H}_2$	(m)	5.7 ± 0.40	9.55 ± 0.22	120–175	$CH_3N_2CH_3$ P	69, 68
$C\mathbf{H}_3ND_2$		9.00 ± 0.20	11.15 ± 0.12	120–175	$CH_3N_2CH_3$ P	69, 68
$CH_3N\mathbf{D}_2$		7.00 ± 0.30	9.61 ± 0.16	120–175	$CH_3N_2CH_3$ P	69, 68
$CD_3N\mathbf{H}_2$		6.00 ± 0.50	9.77 ± 0.28	120–175	$CH_3N_2CH_3$ P	69, 68
$C\mathbf{D}_3NH_2$		10.10 ± 0.30	10.86 ± 0.16	120–175	$CH_3N_2CH_3$ P	69, 68
$C_2H_5NH_2$		7.1	11.2	125–157	D.T.B.P. T	67
		7.3 ± 0.3	10.89 ± 0.18	110–180	$CH_3N_2CH_3$ P	75
$C\mathbf{H}_3CH_2NH_2$		$k = 6.3 \times 10^5$		150	$CH_3N_2CH_3$ P	75

Metathetical Reactions of Methyl Radicals – Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
$CH_3C\mathbf{H}_2NH_2$		8.1	11.2	110–180	$CH_3N_2CH_3$ P	75
$CH_3CH_2N\mathbf{H}_2$		6.5	9.9	110–180	$CH_3N_2CH_3$ P	75
$CH_3CH_2N\mathbf{D}_2$		7.6 ± 0.4	10.04 ± 0.21	110–180	$CH_3N_2CH_3$ P	75
$C\mathbf{D}_3CH_2ND_2$		$k = 1.3 \times 10^5$		150	$CH_3N_2CH_3$ P	75
Amines (secondary)						
$(CH_3)_2NH$		7.2	11.7	125–157	D.T.B.P. P	67
		7.00 ± 0.30	11.20 ± 0.13	120–180	$CH_3N_2CH_3$ P	70
	(y)	7.2 ± 0.4	11.3	184–341	CD_3COCD_3 P	43
$(CH_3)_2N\mathbf{H}$		6.40 ± 0.30	10.81 ± 0.21	120–175	$CH_3N_2CH_3$ P	70
$(C\mathbf{H}_3)_2ND$		8.70 ± 0.60	11.46 ± 0.28	120–175	$CH_3N_2CH_3$ P	70
$(CH_3)_2N\mathbf{D}$		7.80 ± 0.40	10.65 ± 0.22	120–175	$CH_3N_2CH_3$ P	70
$(C_2H_5)_2NH$		7.2	11.8	125–157	D.T.B.P. T	67
	(n)	5.7 ± 1.0	10.7	123–260	CH_3COCH_3 P	71
$((CH_3)_2CH)_2NH$		7.8	12.0	125–157	D.T.B.P. T	67
Amines (tertiary)						
$(CH_3)_3N$		8.0	11.4	132–269	CH_3COCH_3 P	71
		8.9 ± 0.1	11.9 ± 0.1	123–232	CH_3COCH_3 P	76
	(y)	8.8 ± 0.4	11.8	193–302	CD_3COCD_3 P	43
$\mathbf{(C_2H_5)_3N}$	(n)	5.3 ± 1.0	10.4	123–260	CH_3COCH_3 P	71
Imines						
$(CH_2)_2NH$		4.8 ± 0.3	10.7	125–157	D.T.B.P. T	77
	(o)	5.28	10.76	100–216	CH_3COCH_3 P	78
		4.77 ± 0.44	10.29 ± 0.23	110–175	$CH_3N_2CH_3$ P	79, 80
	(y)	5.4	10.94	120–260	CD_3COCD_3 P	78
$(C\mathbf{H}_2)_2NH$	(m)	10.10 ± 2.80	11.44 ± 1.48	110–175	$CH_3N_2CH_3$ P	79, 80
$(CH_2)_2N\mathbf{H}$		4.57 ± 0.10	10.17 ± 0.05	110–175	$CH_3N_2CH_3$ P	79, 80
$(CH_2)_2N\mathbf{D}$		6.34 ± 0.21	10.17 ± 0.13	110–175	$CH_3N_2CH_3$ P	79, 80
$(CH_2)_2NC(CH_3)_3$		6.6	9.6	125–157	D.T.B.P. T	67
$CH_3CH{:}NC(CH_3)_3$		7.8	11.1	125–157	D.T.B.P. T	67
Amides, azines, etc.						
$HCONH_2$		6.6	10.5	170–247	CH_3COCH_3 P	81
$HCONHCH_3$		7.6	10.9	161–287	CH_3COCH_3 P	81
$HCON(CH_3)_2$		8.3	11.4	120–298	CH_3COCH_3 P	81

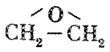
Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
CH_3CONH_2	(q)	9.2 ± 0.3	10.8	144–224	CH_3CONH_2 P	82
$CH_3CON(CH_3)_2$		8.3 ± 0.2	11.3 ± 0.1	106–232	CH_3COCH_3 P	76
$(CH_3)_2NCON(CH_3)_2$		7.3 ± 0.2	11.0 ± 0.1	108–235	CH_3COCH_3 P	76
CH_3ONH_2		4.53 ± 0.25	10.70 ± 0.15	70–190	$CH_3N_2CH_3$ P	83
CH_3OND_2		5.88 ± 0.22	10.55 ± 0.12	70–190	$CH_3N_2CH_3$ P	83
$(CH_3)_2N.NH_2$		5.80 ± 0.20	11.34 ± 0.12	110–180	$CH_3N_2CH_3$ P	68
$(CH_3)_2N.NH_2$	(r)	8.5	11.6	110–180	$CH_3N_2CH_3$ P	68
$CH_3CH{:}NN{:}CHCH_3$		6.1	10.5	125–157	D.T.B.P. T	67
$CH_3N_2CH_3$		7.6 ± 0.3	11.1	60–182	$CH_3N_2CH_3$ P	84
		7.3	10.49	25–150	$CH_3N_2CH_3$ P	85
		6.86 ± 0.18	10.37	−47–50	$CH_3N_2CH_3$ P	86
		8.4 ± 0.3	11.40	80–180	$CH_3N_2CH_3$ P	87
	(s)	7.83 ± 0.08	10.97 ± 0.04	70–190	$CH_3N_2CH_3$ P	83
		8.7	11.47	50–180	$CH_3N_2CH_3$ P	89
$CH_3N{:}N(O)CH_3$		6 ± 2		27–121	$CH_3N{:}N(O)CH_3$ P	90
Aldehydes						
HCHO		$k=4.7\times10^7$		120	CH_3COCH_3/O_2 P	91
		6.2 ± 0.3	11.06	80–180	$CH_3N_2CH_3$ P	87
		6.6	11.25	111–146	D.T.B.P. T	37
DCDO		7.9 ± 0.3	11.15	80–180	$CH_3N_2CH_3$ P	87
CH_3CHO		7.9 ± 0.3	12.15	124–156	D.T.B.P. T	92
		6.8	11.5	91–165	$CH_3N_2CH_3$ P	93
		8.5	12.4	133–291	CH_3CHO P	94
		8.7		109–345	CH_3CHO P	95
		7.6 ± 0.2	11.9 ± 0.1	119–175	D.T.B.P. T	96
		6.8	11.50	25–250	$CH_3N_2CH_3$ P	97
	(y) (f)	6.5 ± 0.3		500–560	CD_3CDO T	29
CH_3CDO		7.9	11.8	27–158	$CH_3N_2CH_3$ P	93
C_2H_5CHO		7.5	11.9	122–156	D.T.B.P. T	99, 92
$CH_2{:}CHCH_2CHO$		10.9	13.3	119–175	D.T.B.P. T	96
$n\text{-}C_3H_7CHO$		7.3 ± 0.3	11.8 ± 0.2	119–175	D.T.B.P. T	96
$n\text{-}C_3F_7CHO$		5.55 ± 0.20	11.20	27–306	$CH_3COCH_3/$ C_3F_7CHO P	98
iso-C_3H_7CHO		8.7 ± 0.3	12.6 ± 0.2	119–175	D.T.B.P. T	96
$n\text{-}C_4H_9CHO$		8.0 ± 0.3	12.1 ± 0.2	119–175	D.T.B.P. T	96
iso-C_4H_9CHO		8.4 ± 0.3	12.3 ± 0.2	119–175	D.T.B.P. T	96

Metathetical Reactions of Methyl Radicals – Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
sec-C$_4$H$_9$CHO		10.4 ± 0.3	13.1 ± 0.3	119–175	D.T.B.P. T	96
t-C$_4$H$_9$CHO		10.2 ± 0.3	13.0 ± 0.3	119–175	D.T.B.P. T	96
Ketones						
CH$_3$COCH$_3$	(t)	9.7 ± 0.1	11.6	121–300	CH$_3$COCH$_3$ P	100
	(h)	9.6 ± 0.4	11.5	100–250	CH$_3$COCH$_3$ P	101
		9.7 ± 0.2	11.8	125–220	CH$_3$COCH$_3$ and Hg(CH$_3$)$_2$ P	102
		9.8	11.59	271–439	CH$_3$COCH$_3$ P	103
		9.5 ± 1.5	11.5	127–175	D.T.B.P. T	104
		9.5 ± 0.3	11.8	130–155	D.T.B.P. T	105
		9.8 ± 0.4	11.60	27–412	CH$_3$COCH$_3$ P	13
		9.56	11.43	132–292	CH$_3$COCH$_3$ P	2, 15
CD$_3$COCD$_2$H	(y) (u)	9.95 ± 0.15	10.74	120–250	CD$_3$COCD$_3$ P	73
	(y) (u)	9.48	9.87	125–200	CD$_3$COCD$_3$ P	74
CD$_3$COCD$_3$	(y)	10.3 ± 0.2	11.6	138–292	CD$_3$COCD$_3$ P	100
	(y)	10.6 ± 0.3	11.8	130–290	CD$_3$COCD$_3$ P	1
	(y)	11.6 ± 0.3	11.8	135–290	CD$_3$COCD$_3$ P	3
	(y)	11.6	12.07	150–250	CD$_3$COCD$_3$ P	30
	(y)	11.44 ± 0.05	11.66 ± 0.03	120–250	CD$_3$COCD$_3$ P	73
	(y)	11.29 ± 0.03	11.57 ± 0.01	125–200	CD$_3$COCD$_3$ P	74
	(y)	10.9 ± 1.0	11.5	130–200	CD$_3$COCD$_3$ P	110
CF$_3$COCH$_3$		8.9	12.0	25–113	CF$_3$COCH$_3$ P	109
CH$_3$COC$_2$H$_5$		7.4	10.6	79–190	CH$_3$COC$_2$H$_5$ P	166
C$_2$H$_5$COC$_2$H$_5$		8.0 ± 0.2	11.8	130–155	D.T.B.P. T	105
		7.0 ± 0.1	11.2	26–134	CH$_3$N$_2$CH$_3$ P	85
	(y)	$k=2.9\times10^7$		141	CD$_3$COCD$_3$ P	111
cyclo-C$_3$H$_5$COCH$_3$		9.6 ± 1		60–170	cyclo-C$_3$H$_5$COCH$_3$ P	112
C$_6$H$_5$COCH$_3$		7.4	10.7	273–407	C$_6$H$_5$COCH$_3$ P	113
CH$_3$COCOCH$_3$		7.1 ± 0.2		28–200	CH$_3$COCOCH$_3$ P	114
		8.5	11.3	140–198	CH$_3$N$_2$CH$_3$ P	116
		7.7		28–200	CH$_3$COCOCH$_3$ P	115
Esters						
HCOOCH$_3$		9.0	10.9	77–230	CH$_3$COCH$_3$ P	117
		9.8	11.3			117
HCOOC$_2$H$_5$		8.2	10.5	77–230	CH$_3$COCH$_3$ P	117
HCOOCH$_2$CH$_2$CH$_3$		7.3	10.1	74–178	CH$_3$COCH$_3$ P	118
HCOOCH(CH$_3$)$_2$		8.9	10.9	94–181	CH$_3$COCH$_3$ P	118
HCOOCH$_2$CH$_2$CH$_2$CH$_3$		8.2	10.6	75–186	CH$_3$COCH$_3$ P	119

Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	*E*	$\log_{10}A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
CH_3COOCH_3		10 ± 0.5	11.2	63–216	CH_3COOCH_3 P	120
CH_3COOCD_3		10 ± 0.5	11.4	151–340	CH_3COCH_3 P	121
		10 ± 0.5	11.4	145–350	CH_3COOCD_3 P	122
CH_3COOCD_3		14 ± 1	11.8	151–274	CH_3COCH_3 P	121
$C_2H_5COOC_2H_5$		8.2	11.3	72–344	$C_2H_5COOC_2H_5$ P	123
$CH_3OCOOCH_3$		8.9 ± 0.7	10.29 ± 0.34	122–253	CH_3COCH_3 P	106
Acids and acid anhydrides						
CH_3COOD		10.2	11.1	105–285	CH_3COOD P	124
$(CH_3CO)_2O$		9.6	11.3	107–196	$(CH_3CO)_2O$ P	125
Ethers and epoxides						
CH_3OCH_3		9.5 ± 0.2	11.5	108–198	CH_3COCH_3 P	43
		8.4 ± 1.5	11.0	100–250	$Hg(CH_3)_2$ P	42
		10 ± 2	11.8	199–292	$CH_3OCH_3 - H$	126
	(y) (f)	10.8 ± 1.0		500–560	CD_3CDO T	29
$(C_2H_5)_2O$		9.75 ± 0.5	12.14	145–179	D.T.B.P. T	127
$[(CH_3)_2CH]_2O$	(y)	7.3 ± 0.4	11.1	179–339	CD_3COCD_3 P	43
 CH_2-CH_2 (O)		9.6 ± 2	11.0	100–200	$Hg(CH_3)_2$ P	42
Peroxides						
CH_3OOCH_3		10.0	12.56	124–185	CH_3OOCH_3 T	128
$((CH_3)CHO)_2$		$k = 4.7 \times 10^5$		26	$((CH_3)_2CHO)_2$ P	129
		$k = 5.3 \times 10^6$		77	$((CH_3)_2CHO)_2$ P	129
$((CH_3)_3CO)_2$		11.7 ± 0.3	12.4	130–155	D.T.B.P. T	105
		14.5 ± 2.5		103–145	D.T.B.P. T	37
Nitriles						
CH_3CN	(y)	10.0 ± 0.5	11.5	100–290	CD_3COCD_3 P	130
C_2H_5CN	(y)	8.5 ± 0.5	11.5	133–297	CD_3COCD_3 P	130
Metal alkyls						
$Hg(CH_3)_2$	(h)	10.8	11.7	25–250	$Hg(CH_3)_2$ P	131
		9.0 ± 0.5	11.3	25–250	$Hg(CH_3)_2$ P	131
		10.8 ± 0.3	11.7	28–251	$Hg(CH_3)_2$ P	33
		10.2 ± 1.0	10.97	160–238	CH_3COCH_3 P	110
		$k = 4.8 \times 10^7$		407	$Hg(CH_3)_2$ T	132
	(y)	10.0 ± 1.0	11.22	125–202	CD_3COCD_3 P	110
$Cd(CH_3)_2$		14 ± 2	12.8	200–275	$Cd(CH_3)_2$ P	5

Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
Halogenated alkanes						
CFH_3	(v)	8.7 ± 0.3	11.6	125–211	CH_3COCH_3 P	133, 135
	(y)	11.8	11.2	193–331	CD_3COCD_3 P	134
CF_2H_2	(v)	6.2 ± 0.3	10.5	129–192	CH_3COCH_3 P	133, 135
	(y)	10.4	11.0	122–301	CD_3COCD_3 P	134
CF_3H	(y)	9.8	9.8	142–293	CD_3COCD_3 P	136, 137
		10.4	10.0	144–309	CD_3COCD_3 P	138
C_2F_5H	(y)	9.7	10.8	135–318	CD_3COCD_3 P	138
C_3F_7H	(y)	9.3	10.6	129–323	CD_3COCD_3 P	138
CH_3Cl	(v)	9.4 ± 0.3	11.8	127–207	CH_3COCH_3 P	133, 135
CH_2Cl_2	(v)	7.2 ± 0.3	11.3	129–211	CH_3COCH_3 P	133, 135
$CHCl_3$	(v)	5.8 ± 0.3	10.8	132–203	CH_3COCH_3 P	133, 135
		6.8		30	CH_3COCH_3 P	139
CH_3Br	(v)	10.1 ± 0.3	12.5	121–208	CH_3COCH_3 P	133, 135
CH_2Br_2	(v)	8.7 ± 0.3	12.2	126–177	CH_3COCH_3 P	133, 135
Hydrides of nitrogen, oxygen, and sulphur						
NH_3		9.8 ± 0.9	11.00 ± 0.42	110–180	$CH_3N_2CH_3$ P	88, 68
		10.0 ± 0.2	10.9 ± 0.1	144–308	CH_3COCH_3 P	76
	(y)	10.0 ± 0.4	10.8	180–339	CD_3COCD_3 P	43
ND_3		10.9 ± 0.9	11.00 ± 0.42	110–180	$CH_3N_2CH_3$ P	88, 68
N_2H_4		5.00 ± 0.1	11.00 ± 0.05	110–180	$CH_3N_2CH_3$ P	88, 68
H_2O	(b)	24.7	13.57			8
H_2S		2.6	11.4	50–140	CH_3COCH_3 P	140
	(w)	3.6	12.1	200–360	CH_3CHO P	141
Hydrogen halides						
HCl		2.3 ± 1	11.6	28–150	CH_3COCH_3 P	142
	(e)	4.51	12.1			143, 144
HI	(x)	2.30	12.50	260–316	CH_3I/HI T	145

FLUORINE ATOM TRANSFER

SF_6		14.1	13.3	157–168	D.T.B.P. T	169

Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	*E*	$\log_{10}A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
			CHLORINE ATOM TRANSFER			
CCl_4		12.9 ± 0.7	13.4	90–145	D.T.B.P. T	146, 147
CCl_3CN		10.4 ± 1.0	12.9	90–145	D.T.B.P. T	147
C_2Cl_6		10.1 ± 0.9	11.8	90–145	D.T.B.P. T	146, 147
$C_6H_5CCl_3$		7.6 ± 0.8	10.3	90–145	D.T.B.P. T	147
CCl_3COCCl_3		9.7 ± 0.8	12.6	90–145	D.T.B.P. T	146, 147
			BROMINE ATOM TRANSFER			
CF_3Br		12.5 ± 1.0	13.3	90–145	D.T.B.P. T	147
CF_2Br_2		6.4 ± 1.0	11.0	90–145	D.T.B.P. T	147
CCl_3Br		7.1 ± 0.9	13.2	90–145	D.T.B.P. T	147
CCl_2Br_2		7.6 ± 1.1	13.8	90–145	D.T.B.P. T	147
CBr_4		7.9 ± 1.1	14.2	90–145	D.T.B.P. T	147
			IODINE ATOM TRANSFER			
I_2		$k = 2 \times 10^{12} - 2 \times 10^{13}$		20	CH_3I/O_2 P	148
		$k = 2.0 \times 10^{16}$		50	CH_2I P	149
	(aa)	1.50	13.0	260–316	CH_3I/HI T	145
		$k = 1.1 \times 10^{13}$		60	CH_3I F.P.	165
CF_3I		7.5 ± 1.0	13.8	90–145	D.T.B.P. T	147
			OXYGEN ATOM TRANSFER			
O_2	(bb)	$k = 5.3 \times 10^8$		498	CH_3COCH_3/O_2 T	150
NO_2		5.7	12.75	1150–1590	CH_3NO_2 ignition	151
			GROUP-TRANSFER REACTIONS			
$^{14}CH_3 + CH_3COCH_3 = {}^{14}CH_3COCH_3 + CH_3$	(ee)	$k = 5.2 \times 10^6$		350	CH_3COCH_3 P	16
$CH_3 + CF_3COCF_3 = CH_3COCF_3 + CF_3$		5.7 ± 1.5	9.3	163–245	$CH_3N_2CH_3$ P, T	171
		6.2 ± 1.0	11.4	85–210	CF_3COCF_3 P	172
		7.0 ± 1.0	11.7	48–240	CH_3COCH_3/CF_3COCF_3 P	173

Metathetical Reactions of Methyl Radicals—Continued

Reactants	Notes	*E*	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
$CH_3 + C_2F_5COC_2F_5 = CH_3COC_2F_5 + C_2F_5$		7 ± 1		184–240	$(C_2F_5)_2CO$ P	174
$CD_3 + CH_3HgCH_3 = CD_3HgCH_3 + CH_3$		$k = 8.9 \times 10^5$		180	CD_3COCD_3 P	175, 176
$CH_3 + CD_3SH = CH_3SH + CD_3$		7.6	10.73	130–200	CH_3COCH_3 P	74
$CH_3 + CF_3COCH_3 = C_2H_6 + CF_3CO$		14		150–350	CF_3COCH_3 P	109
$CH_3 + CH_3COCOCH_3 = CH_3COCH_3 + CH_3CO$		5.6	10.7	100–200	$CH_3COCOCH_3$ P	114
		6.6		100–200	$CH_3COCOCH_3$ P	115
$CH_3 + CH_3CH{:}CHCHO = CH_3CH{:}CHCH_3 + CHO$		7.45 ± 1.30	11.8 ± 0.4	120–250	CH_3COCH_3 P	177
$CH_3 + CH_3HgCH_3 = C_2H_6 + (Hg + CH_3)$		1.0	7	175–220	CH_3HgCH_3 P	131, 178

Ratios of Rate Constants (Methyl Radicals)

(i) Reactions with halogens and hydrogen halides.

Reaction	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°C		
(1) $CH_3 + HBr = CH_4 + Br$ (2) $CH_3 + Br_2 = CH_3Br + Br$		2.0	−0.7		37–210	CH_4/Br/HBr P	167, 168
(1) $CH_3 + HI = CH_4 + I$ (2) $CH_3 + I_2 = CH_3I + I$				0.15	280	CH_3I/HI T	152, 154
				0.13 ± 0.03	270–310	CH_3I/HI T	153, 154
		1.3 ± 0.5	−0.38		126–295	CH_3COCH_3 P	155
		0.8 ± 1.0	−0.50 ± 0.40		260–316	CH_3I/HI T	145
		0.75	−0.64		83–192	CH_3I/HI P	164
(1) $CH_3 + HBr = CH_4 + Br$ (2) $CH_3 + I_2 = CH_3I + I$		0.8 ± 0.3			60	$CH_3I/HBr/I_2$ P	163
		1.37 ± 0.26	−0.30 ± 0.13		80–164	CH_3COCH_3 P	156
		0.95	−0.88		83–192	CH_3I/HBr P	164
(1) $CH_3 + HBr = CH_4 + Br$ (2) $CH_3 + HI = CH_4 + I$	(cc)	1.1 ± 0.4		0.15	25	CH_3I/HBr P	157

Ratios of Rate Constants (Methyl Radicals)—Continued

(i) Reactions with halogens and hydrogen halides.—Continued

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source		Reference
		(kcal mole⁻¹)			°C			
(1) $CH_3+CH_3I=CH_4+CH_2I$ (2) $CH_3+HI=CH_4+I$				0.03	270–310	CH_3I/HI	T	153, 154
(1) $CH_3+HCl=CH_4+Cl$ (2) $CH_3+I_2=CH_3I+I$	(dd)	2.4	−1.46		98–160	CH_3I/HCl	P	164
(1) $CH_3+I_2=CH_3I+I$ (2) $CH_3+NO=CH_3NO$				6	25	CH_3I/NO	P	158
(1) $CH_3+CH_4=CH_4+CH_3$ (2) $CH_3+I_2=CH_3I+I$		6.5 ± 2	−3.8		30–252	$CH_3I/CH_4/I_2$	P	161

(ii) Miscellaneous reactions.

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source		Reference
		(kcal mole⁻¹)			°C			
(1) $CH_3+CH_3CD_3=CH_3D+CH_3CD_2$ (2) $CH_3+CH_3CD_3=CH_4+CH_2CD_3$		0.6 ± 0.04	−0.32		328–424	$CH_3N_2CH_3$	T	159, 27
(1) $CH_3+CH_3CD_2CH_3=CH_3D+CH_3CDCH_3$ (2) $CH_3+CH_3CD_2CH_3=CH_4+CH_2CD_2CH_3$		−1.7	−0.66		312–421	$CH_3N_2CH_3$	T	159, 27
(1) $CH_3+(CH_3)_3CD=CH_3D+(CH_3)_3C$ (2) $CH_3+(CH_3)_3CD=CH_4+CH_2(CH_3)_2CD$		−2.3	−0.51		305–359	$CH_3N_2CH_3$	T	159, 27
(1) $CD_3+CD_2COCD_2CH_2CH_3=CD_4+[C_5D_4H_5O]$ (2) $CD_3+CD_3COCD_2CH_2CH_3=CD_3H+[C_5D_5H_4O]$		0.7			35–144	$CD_3COCD_2CH_2CH_3$	P, T	36
(1) $CH_3+CH_3OCH_2CH_3=CH_4+[C_3H_7O]$ (2) $CH_3+CH_3OCH_3=CH_4+CH_2OCH_3$				4 to 12	525	CH_3OCH_3	T	160
(1) $CH_3+HCHO=CH_4+HCO$ (2) $CH_3+CH_3OCH_3=CH_4+CH_2OCH_3$				3	507	CH_3OCH_3	T	9
(1) $CH_3+O_2=HCHO+OH$ (2) $CH_3+O_2+M=CH_3O_2+M$				1.0×10^{-8} k_1/k_2 [M] $=0.49$	25 162	CH_3I/O_2 P $CH_3N_2CH_3/O_2$	 P	170 162

Notes

(a) When corrected, these activation energies are 10.5 and 12.2 kcal respectively (see ref. 11).

(b) This value was used (without a source being quoted), in the range 1000–1500 °C.

(c) Use of the more recent activation energy for CH_3+CH_3CHO gives $E=12.0$ kcal (see ref. 11).

(d) For a re-analysis of these results see reference 15.

(e) Calculated from the reverse reaction.

(f) Assuming an activation energy of 9.2 kcal/mole for the reaction $CD_3+CD_3CDO=CD_4+CD_3CO$.

(g) Assuming $k=10^{12.3}$ exp $(-13{,}600/RT)$ for the reaction $CH_3+C_2D_6=CH_3D+C_2D_5$.

(h) The quantities were not calculated in this manner by the original authors.

(i) Assuming $k=10^{11.7}$ exp $(-10{,}800/RT)$ for the reaction $CH_3+CH_3HgCH_3=CH_4+CH_3HgCH_2$.

(j) Pyrolysis of a series of methyl metal derivatives.

(k) Assuming $k=10^{11.8}$ exp $(-12{,}000/RT)$ for the reaction $CH_3+D_2=CH_3D+D$.

(l) No distinction made between *o*, *m*, and *p* xylenes.

(m) Calculated assuming a zero secondary isotope effect.

(n) These are not the values quoted by the authors, but corrected (see ref. 67) for arithmetical errors.

(o) No significant quantities of CH_3D were formed, when acetone was photolyzed in presence of $(CD_2)_2NH$.

(p) These values are doubtful.

(q) No significant quantities of CH_3D formed during the photolysis of CH_3COND_2.

(r) Calculated assuming the parameters for abstraction from the $-NH_2$ group, are as for those in hydrazine.

(s) See also references 69, 70, 75, 79, 80, and 88.

(t) Several other studies are in excellent agreement with those listed. See references 1, 23, 59, 65, 74, 106, 107, and 108.

(u) "A" factor doubtful.

(v) The results for CCl_4, CH_2Cl_2, and CH_3Cl are invalid: the others are to be regarded with some suspicion (see ref. 135).

(w) Assuming $k=10^{11.9}$ exp $(-7600/RT)$ for the reaction $CH_3+CH_3CHO=CH_4+CH_3CO$.

(x) The authors consider the activation energy to be ~ 1 kcal too high.

(y) The attacking radical is CD_3.

(z) The variations reported within these series may be spurious as variations in E are compensated by variations in A.

(aa) The authors consider the activation energy to be ~ 1 kcal too high.

(bb) The products of this reaction are HCHO and OH.

(cc) Activation energy difference calculated assuming identical A factors.

(dd) "Hot" methyl radicals may have played an important part in this system.

(ee) Assuming $k=10^{11.6}$ exp $(-9800/RT)$ for the reaction $CH_3+CH_3COCH_3=CH_4+CH_2COCH_3$.

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Difluoromethylene Radicals

Reaction	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$CF_2+O_2=CO+2F+O$		14.98	12.30 *e*	1307–2117	C_2F_4/O_2 S.T.^{r}	1

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Trifluoromethyl Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
Hydrogen		*(kcal mole⁻¹)*	*(mole⁻¹ cc. sec⁻¹)*	°C		
H_2		9.5 ± 0.7	11.86	59–158	CF_3COCF_3	1
		8.8	11.60	219–346	$CF_3N_2CF_3$	2
	(a)	25.1	11.89	832–1011		3
$\mathbf{H}\mathrm{D}$		10.5 ± 1.5	11.78	102–174	CF_3COCF_3	1
$\mathrm{H}\mathbf{D}$		10.2 ± 1.5	11.35	102–174	CF_3COCF_3	1
D_2		10.2 ± 0.7	11.45	86–196	CF_3COCF_3	1
		9.7	11.44	220–346	$CF_3N_2CF_3$	2
Alkanes						
CH_4		10.3 ± 0.5	11.70	122–251	CF_3COCF_3	4
		10.6	11.73	170–310	CF_3CHO	5
		9.5 ± 2	11.2	30–350	CF_3COCF_3	6
		11.0 ± 0.1	11.98	84–261	CF_3COCF_3	7
		11.3 ± 0.5	11.96 ± 0.22	153–295	CF_3COCF_3	8
		11.0	11.98			
$\mathrm{C}\mathbf{H}\mathrm{D}_3$		10.5 ± 0.3	11.04	55–354	CF_3COCF_3	9
$\mathrm{CH}\mathbf{D}_3$		12.75 ± 0.3	11.33	55–354	CF_3COCF_3	9
CD_4		12.1 ± 2.1	11.18	106–287	CF_3COCF_3	7
C_2H_6		7.5 ± 0.5	11.68	81–216	CF_3COCF_3	4
		7.5	11.63	220–350	$CF_3N_2CF_3$	2
C_3H_8		6.2	11.67	200–310	$CF_3N_2CF_3$	2
		6.5 ± 0.5	11.75	27–119	CF_3COCF_3	10
n-C_4H_{10}		5.1 ± 0.3	11.15	29–93	CF_3COCF_3	10
		5.5 ± 1.0	10.9	30–350	CF_3COCF_3	6
		5.3	11.46	200–310	$CF_3N_2CF_3$	2
iso-C_4H_{10}		4.7 ± 0.3	11.15	28–84	CF_3COCF_3	10
		4.7	11.17	170–240	CF_3CHO	5
$(\mathrm{CH_3})_3\mathrm{C}\mathbf{D}$		7.4 ± 1.0	12.48	62–208	CF_3COCF_3	7
neo-C_5H_{12}		7.6	11.76	250–320	$CF_3N_2CF_3$	2
$CH_3C(CH_3)_2CH_2CH_3$		1.7	10.22	250–300	$CF_3N_2CF_3$	2
Cyclo-Alkanes						
cyclo-C_5H_{10}		4.7	11.54	210–300	$CF_3N_2CF_3$	2
cyclo-C_6H_{12}		5.0 ± 0.2	11.44	19–91	CF_3COCF_3	11

Trifluoromethyl Radicals – Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		(kcal mole^{-1})	*(mole^{-1} cc. sec^{-1})*	°C		
Aromatic hydrocarbons						
C_6H_6		6.3 ± 0.20	11.35	23–86	CF_3COCF_3	11
	(b)	7.7	11.44		$CF_3N_2CF_3$	2
$C_6H_5CH_3$	(b)	6.0	11.33		$CF_3N_2CF_3$	2
		5.91 ± 0.30	11.59 ± 0.20	27–110	CF_3COCF_3	12
		5.37 ± 0.26	11.10	25–81	CF_3COCF_3	11
$C_6H_5CD_3$		5.8 ± 0.4	10.13	22–72	CF_3COCF_3	13
o-$C_6H_4(CH_3)_2$		5.55 ± 0.54	11.68	37–68	CF_3COCF_3	11
Halogenated Aromatics						
C_6H_5Cl		5.5 ± 0.3	10.56	20–118	CF_3COCF_3	14
C_6H_5Br		5.9 ± 0.5	11.53	23–95	CF_3COCF_3	14
C_6H_5I		4.5 ± 0.1	10.86	75–150	CF_3COCF_3	14
$C_6H_5CH_2Cl$		8.0 ± 0.3	12.46	67–151	CF_3COCF_3	14
$C_6H_5CCl_3$		8.8 ± 0.6	12.55	104–171	CF_3COCF_3	14
$C_6F_5CH_3$		6.38	10.75		CF_3COCF_3	15
Aldehydes						
CH_3CHO		4.2	10.84	170–250	CF_3CHO	5
CF_3CHO		8.4	11.73	150–400	CF_3CHO	5
Ketones						
CH_3COCH_3		8.0	11.51	250–320	$CF_3N_2CF_3$	2
		6.9 ± 0.1	10.77	29–169	CF_3COCF_3	16
		8.27 ± 0.17	11.52 ± 0.08	85–240	CF_3COCF_3	17, 16
CF_3COCH_3		6.6	11.3	25–350	CF_3COCH_3	18
$C_6H_5COCF_3$		7.2 ± 0.5	9.7	158–304	$C_6H_5COCF_3$	19
Halogenated Methanes						
CH_3Cl		10.6 ± 0.2	12.11 ± 0.08	144–400	CF_3COCF_3	8
CH_2Cl_2		7.6 ± 0.1	11.19 ± 0.08	85–204	CF_3COCF_3	20
$CHCl_3$		6.6 ± 0.1	11.04 ± 0.06	94–296	CF_3COCF_3	20
		5.3 ± 0.1	10.16 ± 0.07	35–338	$CF_3N_2CF_3$	21
		6.3 ± 0.6	11.98	118–251	CF_3COCF_3	7

Trifluoromethyl Radicals—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		(kcal mole^{-1})	*(mole^{-1} cc. sec^{-1})*	°C		
$CDCl_3$		9.0 ± 0.4	11.78	65–264	CF_3COCF_3	7
CH_3Br	(d)	10.9 ± 0.3	12.19 ± 0.14	150–260	CF_3COCF_3	8
	(e)	9.9 ± 0.1	11.63 ± 0.06	150–260	CF_3COCF_3	8
CH_3I		7.5 ± 0.3	10.63 ± 0.16	55–210	CF_3COCF_3	8
Hydrogen halides and hydrogen sulphide						
HCl		5.1 ± 0.5	11.05	20–205	CF_3COCF_3	26
HBr		2.9 ± 0.5	11.78		CF_3COCF_3	26
		$k = 3.0 \times 10^8$		26	CF_3COCF_3	22
H_2S		3.83 ± 0.26	11.65 ± 0.16	63–100	CF_3COCF_3	27

CHLORINE ATOM TRANSFER (i)

Cl_2		3.6 ± 0.5	12.89	126–235	CF_3COCF_3	26
CH_3Cl		$\geqslant 17$			CF_3COCF_3	20
CH_2Cl_2		11.8 ± 0.7	11.49 ± 0.1	306–449	CF_3COCF_3	20
$CHCl_3$	(f)	12.0 ± 0.2	12.08 ± 0.1	95–296	CF_3COCF_3	20
		11.0 ± 0.4	11.33 ± 0.2	35–338	$CF_3N_2CF_3$	21
CCl_4		9.3 ± 0.4	11.79 ± 0.2	122–288	$CF_3N_2CF_3$	21
		10.4 ± 0.1	12.57 ± 0.04	96–240	CF_3COCF_3	20
C_6H_5Cl		$\geqslant 13$		20–118	CF_3COCF_3	14
$C_6H_5CH_2Cl$		$\geqslant 13$		67–151	CF_3COCF_3	14
$C_6H_5CCl_3$		9.7 ± 0.5	12.49	104–171	CF_3COCF_3	14

BROMINE ATOM TRANSFER

Br_2		0.7 ± 0.5	12.36	178–327	CF_3COCF_3	26
CH_3Br	(d)	8.4 ± 0.1	10.83 ± 0.06	150–260	CF_3COCF_3	8
	(e)	8.1 ± 0.2	10.41 ± 0.10	150–260	CF_3COCF_3	8
C_6H_5Br	(g)	1.7 ± 1.1	7.91	23–95	CF_3COCF_3	14
C_6F_5Br	(g)	0.3 ± 0.6	7.38	39–107	CF_3COCF_3	14
HBr	(a)	84.2	10.71	832–1011		23

Trifluoromethyl Radicals—Continued

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(kcal mole^{-1})	*(mole^{-1} cc. sec^{-1})*	*°C*		
		IODINE ATOM TRANSFER				
I_2		0.0 ± 0.5	12.42		CF_3COCF_3	26
CH_3I		3.3 ± 0.15	9.59 ± 0.08	55–210	CF_3COCF_3	8
C_6H_5I		3.1 ± 0.6	10.33	75–150	CF_3COCF_3	14
		OXYGEN ATOM TRANSFER				
N_2O	(h)	24.0	13.15	316–375	CF_3COCF_3	24

Ratios of Rate Constants (Trifluoromethyl Radicals)

Reaction	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	Temperature range	Radical source	Reference
		(kcal mole^{-1})		*°C*		
(1) $CF_3 + Br_2 = CF_3Br + Br$ (2) $CF_3 + HBr = CF_3H + Br$		-0.52 ± 1.88	0.93 ± 0.60	361–431	CF_3H thermal bromination	22
		-2.17 ± 0.16	0.58 ± 0.08	55–334	CF_3COCF_3	25
(1) $CF_3 + I_2 = CF_3I + I$ (2) $CF_3 + HBr = CF_3H + Br$		-2.98 ± 0.12	0.64 ± 0.06	85–230	CF_3COCF_3	25
(1) $CF_3 + CHD_3 = CF_3H + CD_3$ (2) $CF_3 + CHD_3 = CF_3D + CHD_2$		-2.2	-0.29	55–354	CF_3COCF_3	9
(1) $CF_3 + CH_2D_2 = CF_3H + CHD_2$ (2) $CF_3 + CH_2D_2 = CF_3D + CH_2D$		$\ln k_1/k_2 = \ln 1.400 + 0.42 \times 10^6/T^2$		727–1067	$CF_3N_2CF_3$	28

Notes

(a) CF_3Br inhibition of H_2/O_2 shock tube ignition.

(b) Values less reliable than others quoted by the same authors.

(c) Results combined with data from reference 16.

(d) At low (25mm Hg) CH_3Br pressures.

(e) At high (180mm Hg) CH_3Br pressures.

(f) This result is preferred to that obtained with $CF_3N_2CF_3$.

(g) "A" factor unreasonable.

(h) Result described as "semi-quantitative."

(i) For data involving fluorine atom transfer, see reference 29.

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Metathetical Reactions of Halogenated Methyl Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
(i) Reactions of CFH_2 Radicals						
Hydrogen atom transfer		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
CFH_2COCFH_2	(a)	8.0 ± 0.1	10.71	100–300	CFH_2COCFH_2 P	1
(ii) Reactions of CF_2Cl Radicals						
Hydrogen atom transfer						
cyclo-C_5H_{10}	(b)	5.3 ± 0.4		50–227	$CF_2ClCOCF_2Cl$ P	2
Chlorine atom transfer						
$CF_2ClCOCF_2Cl$	(b) (b)	4 ± 1 ~ 3		20–180 20–184	$CF_2ClCOCF_2Cl$ P $CF_2ClCOCF_2Cl$ P	3 4
(iii) Reactions of CCl_3 Radicals						
Hydrogen atom transfer						
H_2	(c)	11.3 ± 0.5	14.86	248–302	CCl_3Br P	5
$\mathbf{CH_3}CH_2CH_2\mathbf{CH_3}$	(d)	11.2	10.1	146–257	CCl_3Br P	6, 7
$CH_3\mathbf{CH_2}\mathbf{CH_2}CH_3$	(d)	7 5	9.9	146–257	CCl_3Br P	6, 7
HBr	(d)	$k = 2.76 \times 10^{11}$		190	CCl_3Br P	6
Chlorine atom transfer						
Cl_2	(d)	5.3	12.86	70–155	$CHCl_3/Cl_2$ P	8, 9
CCl_3Br		18.6 ± 1 17.4 ± 1		225–294 248–302	CCl_3Br P CCl_3Br P	10 5
CCl_3COCCl_3		7 ± 1		107–252	CCl_3COCCl_3 P	11

Ratios of Rate Constants (Trichloromethyl Radicals)

Reactants	Notes	E_1-E_2	$\log_{10}A_1/A_2$	Temperature range	Radical source	Reference
		(kcal mole^{-1})		°*C*		
(1) $CCl_3+n\text{-}C_4H_{10}$ $=\text{sec-}C_4H_9+CCl_3H$ (2) $CCl_3+n\text{-}C_4H_{10}$ $=p\text{-}C_4H_9+CCl_3H$		-3.08 ± 0.46	0.43 ± 0.25	197–294	CCl_3Br P	7
(1) $CCl_3+i\text{-}C_4H_{10}$ $=(CH_3)_3C+CCl_3H$ (2) $CCl_3+n\text{-}C_4H_{10}$ $=\text{sec-}C_4H_9+CCl_3H$		-2.40	0.30	132–189	CCl_3Br P	7

Notes

(a) Calculated assuming $k=10^{14}$ cm^3 mole^{-1} sec^{-1} for the combination of CFH_2 radicals.

(b) Calculated assuming $k=10^{14}$ cm^3 mole^{-1} sec^{-1} for the combination of CF_2Cl radicals.

(c) Calculated assuming $k=10^{10.7}$ cm^3 mole^{-1} sec^{-1} for the combination of CCl_3 radicals.

(d) Calculated assuming $k=10^{11.36}$ cm^3 mole^{-1} sec^{-1} for the combination of CCl_3 radicals.

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Relative Rate Constants (Formyl Radicals)

Reactants	Notes	E_1-E_2	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)			°*C*		
(1) $HCO+NO_2=HNO_2+CO$ (2) $HCO+NO_2=HCO_2+NO$		0.65	0.5		100–220	CH_2O/NO_2 T	1, 2
(1) $HCO(+M)=CO+H(+M)$ (2) $HCO+O_2=CO+HO_2$				2.7×10^{-9} cm^{-3} mole	36	CH_3COCH_3/O_2 P	3

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Metathetical Reactions of Methoxy Radicals

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	References
HYDROGEN ATOM TRANSFER						
Alkanes		*(kcal mole^{-1})*	*(cm^3 mole^{-1} sec^{-1})*	°C		
CH_4	(a)	11.0	11.8	125–250		15
C_2H_6	(b)	7.1	11.5	200–400	CH_3OOCH_3 T	1, 2, 3
C_3H_8	(b)	5.2	11.3	200–400	CH_3OOCH_3 T	1, 2, 3
n-C_4H_{10}	(c) (b)	2.9	10.5	200–400	CH_3OOCH_3 T	1, 2, 3
iso-C_4H_{10}	(b)	4.1	11.0	190–260	CH_3OOCH_3 T	1, 2, 3
$(CH_3)_4C$	(b)	7.3	11.8	200–300	CH_3OOCH_3 T	1, 2
Cyclo-Alkanes						
cyclo-C_3H_6	(b)	9.7	12.2	200–400	CH_3OOCH_3 T	1, 2
Esters						
$HCOOCH_3$		8.2	12.2	124–185	CH_3OOCH_3 T	4, 5
CH_3COOCH_3		~4.5		63–216	CH_3COOCH_3 P	6, 14
CH_3COOCD_3	(d)	~5		30–201	CH_3COOCD_3 P	7, 14

Ratios of Rate Constants (Methoxy Radicals)

Reactants	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	Temperature range	Radical source	References
		(kcal mole^{-1})		°C		
(1) $CH_3O + CH_3OH = CH_3OH + CH_2OH$ (2) $CH_3O + HCHO = CH_3OH + HCO$		3.0 − 4.3		155–180	CH_3OOCH_3 P	8, 12
(1) $CH_3O + HCHO = CH_3OH + HCO$ (2) $2CH_3O = CH_3OH + HCHO$	(f)	$k_1/k_2^{1/2} = 10^{3.68}$ exp $(-3000/RT)$		50–135	D.T.B.P. T, P	9
(1) $CH_3O + O_2 = CH_2O + HO_2$ (2) $2CH_3O = CH_3OH + CH_2O$	(f)	$k_1/k_2^{1/2} = 0.59$		room temp.	CH_3I/O_2 P	10
(1) $CH_3 + CH_2(OCH_3)_2 = CH_3OH + [C_3H_7O_2]$ (2) $CH_3O = H + CO + H_2$		$k_1/k_2 = 1.14 \times 10^5$ cm^3 mole^{-1}		459	$CH_2(OCH_3)_2$ T	11

Notes

(a) Calculated from the back reaction.

(b) The *A* factors were deduced by a semi-empirical method by Berces and Trotman-Dickenson (ref. 1). The original work contained an arithmetical mistake that resulted in an overestimate of log *A* of 0.3 units.

(c) This value seems likely to be incorrect.

(d) The reactant radical in this case is CD_3O.

(e) For further data on methoxy radicals see reference 13.

(f) Units are $cm^{3/2}$ $mole^{-1/2}$ $sec^{-1/2}$.

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Metathetical Reactions of Methylthio Radicals

Reactants	Note	E	$\log_{10} A$	Temperature range	Radical source		References
		HYDROGEN ATOM TRANSFER					
		(*kcal mole^{-1}*)	(*cm^3 mole^{-1} sec^{-1}*)	°*C*			
CH_4	(a)	18.2	12.1	130–200			1
CH_3CHO		6.8	11.9	189–396	CH_3CHO/CH_3SH	P	2
		4.8	12.0	400–440	CH_3CHO/CH_3SH	T	3

Notes

(a) Calculated from the reverse reactions.

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Reactions of Chloroformyl Radicals

Reactions	Notes	E	$\log_{10} A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
$COCl + Cl_2 = COCl_2 + Cl$		2.96	12.4	25–55	CO/Cl_2 P	1
	(a)	3.1	10.8	15–450		5
$COCl + NOCl = Cl_2 + CO + NO$ (or $COCl_2 + NO$)		1.14	13.68	25–55	$CO/Cl_2/NOCl$ P	2
$COCl + O_2 = CO_2 + ClO$		3.3	10.9	20–200	$Cl_2/O_2/CO$ P	3, 4

Notes

(a) Review of literature data.

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Metathetical Reactions of Cyano Radicals

Reactions	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$H_2+CN=HCN+H$		~7			D.F.	1
$ClCN+CN=C_2N_2+Cl$		6.0	13.05	1727–2527	ClCN ... S.T.	2
$C_2N_2+CN=$ products		2.1	10.86	28–174	C_2N_2 F.P.	3
$O_2+CN=NCO+O$		$k=4.6\times10^{12}$		room temp.	C_2N_2/O_2 F.P.	5
		$k=5.5\times10^{12}$		room temp.	C_2N_2/O_2 F.P.	3

Ratios of Rate Constants

Reactions	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)			°*C*		
(1) $CH_4+CN=CH_3+HCN$ (2) $C_2H_6+CN=C_2H_5+HCN$		3.7 ±0.2	1.31		30–150	ICN P	4
(1) $C_2H_6+CN=C_2H_5+HCN$ (2) $C_3H_8+CN=n\text{-}C_3H_7+HCN$		−0.1 ±0.2	0.00		30–150	ICN P	4
(1) $C_2H_6+CN=C_2H_5+HCN$ (2) $C_3H_8+CN=i\text{-}C_3H_7+HCN$		−0.1 ±0.3	0.04		30–150	ICN P	4
(1) $C_3H_8+CN=n\text{-}C_3H_7+HCN$ (2) $C_3H_8+CN=i\text{-}C_3H_7+HCN$		−0.1 ±0.3	0.08		30–150	ICN P	4

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Ratios of Rate Constants (Ethynyl Radicals)

(i) Reactions of the type (1) $C_2H + RH = C_2H_2 + R$
(2) $C_2H + BrC_2H = C_4H_2 + Br$.

RH	Notes	k_1/k_2	Temperature	Radical source	References
Alkanes			°C		
CH_4		0.020	27	BrC_2H P	1
C_2H_6		0.40	27	BrC_2H P	1
n-C_4H_{10}		1.05	27	BrC_2H P	1
iso-C_4H_{10}		1.25	27	BrC_2H P	1
$(CH_3)_4C$		1.1	27	BrC_2H P	1
$(CH_3)_3C.C(CH_3)_3$		1.2	27	BrC_2H P	1
Cyclo-alkanes					
cyclo-C_3H_6		0.21	27	BrC_2H P	1
cyclo-C_4H_8		1.35	27	BrC_2H P	1
spiro-C_5H_8		0.64	27	BrC_2H P	1
cyclo-C_5H_{10}		2.1	27	BrC_2H P	1
cyclo-C_6H_{12}		3.2	27	BrC_2H P	1
cyclo-C_6D_{12}		2.3	27	BrC_2H P	1
Halogenated alkanes					
C_2H_5Cl		0.14	27	BrC_2H P	1

(ii) Reactions of the type (1) $C_2H + RH = C_2H_2 + R$
(2) $C_2H + CH_2{:}CHCH_2CH_3 = C_2H_2 + C_4H_7$

RH	Notes	k_1/k_2	Temperature	Radical source	Reference
Alkenes			°C		
$CH_2{:}CHCH_3$		0.63	27	BrC_2H P	2
cis-$CH_3CH{:}CHCH_3$		1.04	27	BrC_2H P	2
trans-$CH_3CH{:}CHCH_3$		1.06	27	BrC_2H P	2
$CH_2{:}C(CH_3)_2$		0.90	27	BrC_2H P	2
$CH_2{:}CHCH_2CH_2CH_3$		1.7	27	BrC_2H P	2
$CH_2{:}CHCH(CH_3)_2$		1.22	27	BrC_2H P	2

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Metathetical Reactions of Ethyl Radicals

Reactants	Notes	*E*	$\log_{10} A$	Temperature range	Radical source	Reference
			HYDROGEN ATOM TRANSFER			
Hydrogen		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
H_2	(a)	11.5 ± 1				1
		4.05	12.19	752–917	H_2/O_2 ignition S.T.	2
	(b)	11.3 ± 0.5	11.51	83–322	$(C_2D_5)_2CO$ P	3
		15.9	12.8			
D_2		13.3 ± 0.5	12.0	54–287	$(C_2H_5)_2CO$ P	1
Alkanes						
n-C_4H_{10}		15.2	11.77	420–530	*n*-C_4H_{10} T	4
	(b)	10.4	11.03	106–325	$(C_2D_5)_2CO$ P	5
i-C_4H_{10}	(b)	8.9	10.62	87–319	$(C_2D_5)_2CO$ P	5
neo-C_5H_{12}	(b)	12.6	11.25	86–324	$(C_2D_5)_2CO$ P	5
cyclo-C_6H_{12}	(b)	10.4 ± 0.5	11.42 ± 0.2	99–293	$(C_2D_5)_2CO$ P	3
n-C_6H_{14}	(b)	10.1 ± 0.5	11.14 ± 0.2	87–252	$(C_2D_5)_2CO$ P	3
n-C_7H_{16}		10.6 ± 0.4	11.69 ± 0.2	124–200	$(C_2H_5)_2CO$ P	6
Alkenes						
1,5-C_6H_{10}		6.3 ± 0.4	10.1 ± 0.2	71–175	$(C_2H_5)_2CO$ P	7
1-C_7H_{14}		8.3 ± 0.5	11.19 ± 0.3	85–200	$(C_2H_5)_2CO$ P	6
1-C_8H_{16}		8.3 ± 0.2	11.19 ± 0.3	85–180	$(C_2H_5)_2CO$ P	6
		7.5 ± 0.5	10.6 ± 0.3	66–152	$(C_2H_5)_2CO$ P	9
trans 4-C_8H_{16}		8.7 ± 1.0	11.5 ± 0.6	85–165	$(C_2H_5)_2CO$ P	6
$(CH_3)_2C{:}CHCH{:}C(CH_3)_2$		7.6 ± 0.4	11.1 ± 0.2	53–147	$(C_2H_5)_2CO$ P	9
Cyclo alkenes						
cyclohexadiene,-1,3.		5.4 ± 0.5	10.6 ± 0.3	25–160	$(C_2H_5)_2CO$ P	9, 8
cyclohexadiene,-1,4.		5.8 ± 0.1	11.3 ± 0.1	50–140	$(C_2H_5)_2CO$ P	10
cyclohexene		8.2 ± 0.5	11.5 ± 0.3	23–250	$(C_2H_5)_2CO$ P	6
		7.5 ± 0.4	10.2 ± 0.2	40–210	$(C_2H_5)_2CO$ P	10
cycloheptatriene		6.5 ± 0.5	10.9 ± 0.3	50–130	$(C_2H_5)_2CO$ P	10
cyclooctatetraene		8.6 ± 1.2	11.6 ± 0.7	50–130	$(C_2H_5)_2CO$ P	10
cyclooctadiene,-1,5.		6.8 ± 0.7	10.9 ± 0.4	60–130	$(C_2H_5)_2CO$ P	10

Metathetical Reactions of Ethyl Radicals—Continued

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
Alkynes						
i-C_7H_{12}		7.6 ± 0.2	10.9 ± 0.1	23–180	$(C_2H_5)_2CO$ P	6
Aldehydes						
C_2H_5CHO		7.6 ± 1.0	11.5	134–156	D.T.B.P. T	11
		5.9	10.8	91–315	C_2H_5CHO P	12
		6.3		100–175	C_2H_5CHO P	12, 13
Ketones						
$CH_3COC_2H_5$		8.0 ± 0.1	11.0	79–234	$CH_3COC_2H_5$ P	16
$(C_2H_5)_2CO$		7.4	10.9	25–225	$(C_2H_5)_2CO$ P	14, 21
		7.6	11.0	41–158	$(C_2H_5)_2N_2$ P	15
		7.8 ± 0.2	11.1 ± 0.1	50–215	$(C_2H_5)_2CO$ P	6
		8.9	11.7	75–170	$(C_2H_5)_2CO$ P	17
$(CH_3CD_2)_2CO$	(c)	11.7	11.4	24–365	$(CH_3CD_2)_2CO$ P	18
$(CH_3CD_2)_2CO$	(c)	8.7	11.6	24–365	$(CH_3CD_2)_2CO$ P	18, 19
		9.2 ± 0.4	11.1 ± 0.1	24–365	$(CH_3CD_2)_2CO$ P	19
$(C_2D_5)_2CO$	(b)	9.6 ± 0.4	11.3	160–314	$(C_2D_5)_2CO$ P	19
		9.0 ± 0.5	10.95	50–324	$(C_2D_5)_2CO$ P	5
$C_2F_5COC_2H_5$		6.8	10.85	100–250	$C_2F_5COC_2H_5$ P	37
$C_3F_7COC_2H_5$		7.2	10.9	80–362	$C_3F_7COC_2H_5$ P	20
Esters						
$HCOOC_2H_5$		7.8	10.6	77–230	CH_3COCH_3 P	17
$C_2H_5COOC_2H_5$		9.8	11.5	108–344	$C_2H_5COOC_2H_5$ P	22
$C_2H_5COOCH_2CH{:}CH_2$		5.8 ± 1.4	9.7 ± 0.8	79–160	$(C_2H_5)_2CO$ P	23
Azo-compounds						
$(C_2H_5)_2N_2$		7.5	10.9	74–178	$(C_2H_5)_2N_2$ P	24
		8.0 ± 0.2	11.4	27–175	$(C_2H_5)_2N_2$ P	25
Metal alkyl						
$(C_2H_5)_2Hg$		6.2	10.3	75–200	$(C_2H_5)_2Hg$ P	26
Hydrogen halide						
HI		1.1	11.92	263–303	HI/C_2H_5I T	27

Metathetical Reactions of Ethyl Radicals—Continued

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
			CHLORINE ATOM TRANSFER			
Cl_2		1.0	13.1			28
			IODINE ATOM TRANSFER			
I_2	(d)	0.2	12.50	263–303	HI/C_2H_5I T	27
			OXYGEN ATOM TRANSFER			
N_2O	(e)	31.0	17.8	553–588	C_2H_6/N_2O T	29

Ratios of Rate Constants (Ethyl Radicals)

Reaction	Notes	E_1-E_2	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(kcal mole^{-1})			°C		
(1) $C_2H_5+HBr=C_2H_6+Br$ (2) $C_2H_5+Br_2=C_2H_5Br+Br$		0	-0.22		30–90	$C_2H_6/Br_2/HBr$ P	30, 36
(1) $C_2H_5+HI=C_2H_6+I$				0.15	260	C_2H_5I/HI T	33, 32
(2) $C_2H_5+I_2=C_2H_5I+I$				0.13 ± 0.03	250–280	C_2H_5I/HI T	31, 32
		0.90	-0.58		263–303	C_2H_5I/HI T	27
(1) $C_2H_5+HBr=C_2H_6+Br$ (2) $C_2H_5+I_2=C_2H_5I+I$		2.29 ± 0.08	0.23 ± 0.04		55–115	$CH_3COC_2H_5$ P	34
(1) $C_2H_5+I_2=C_2H_5I+I$ (2) $C_2H_5+O_2=C_2H_5O_2$				13	25	C_2H_5I/O_2 P	35
(1) $C_2H_5+I_2=C_2H_5I+I$ (2) $C_2H_5+NO=C_2H_5NO$				7	25	C_2H_5I/NO P	35

Notes

(a) Estimated from the reaction $D_2+C_2H_5$, assuming the difference in activation energies to be equal to the difference of the zero-point energies.

(b) The attacking radical is C_2D_5.

(c) The attacking radical is CH_3CD_2.

(d) Calculated, assuming the activation energy of 0.2 kcal/mole.

(e) This *A* factor seems improbably high.

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Perfluoroethyl Radicals

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
		(*kcal mole*$^{-1}$)	(*mole*$^{-1}$ *cc sec*$^{-1}$)	°C		
H_2		11.9	12.72	137–237	$(C_2F_5)_2CO$	1
	(a)	12.4 ± 0.2	13.20	146–313	C_2F_5CHO	2
D_2	(a)	12.6 ± 0.2	12.45	135–339	C_2F_5CHO	2
		14.1 ± 0.3	13.08	154–259	$(C_2F_5)_2N_2$	3
CH_4		10.6	11.62	150–272	$(C_2F_5)_2CO$	1
C_2H_6		8.7 ± 0.2	12.18	84–226	$(C_2F_5)_2N_2$	3
cyclo-C_6H_{12}		6.0 ± 0.2	12.18	28–132	$(C_2F_5)_2N_2$	3
CF_3CHO		9.7 ± 0.2	12.40	138–220	$(C_2F_5)_2N_2$	3
C_2F_5CHO		4.5 ± 0.2	10.49	27–307	C_2F_5CHO	4
		4.9 ± 0.2	10.74	135–339	C_2F_5CHO	2
CH_3COCH_3		8.4 ± 0.2	11.71	82–220	$(C_2F_5)_2N_2$	3
$C_2F_5COC_2H_5$		5.6 ± 0.2	11.34	50–250	$C_2F_5COC_2H_5$	5

Notes

(a) These results are less reliable than those obtained from perfluoro ketone systems.

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Metathetical Reactions of Halogenated Ethyl Radicals

Reactions	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$CH_2CH_2Cl + Cl_2$ $= CH_2ClCH_2Cl + Cl$		0			$CH_2{:}CH_2/Cl_2$ P	1, 2
$C_2H_3Cl_2 + Cl_2$ $= CH_2ClCHCl_2 + Cl$	(c)	0.92 ± 0.05	11.75 ± 0.2	25–55	$CH_2{:}CHCl/Cl_2$ P	1, 2, 3
$CHCl_2CHCl + Cl_2$ $= CHCl_2CHCl_2 + Cl$		2.74 ± 0.6	11.7 ± 0.3	30–65	cis-$CHCl{:}CHCl/Cl_2$ P	4, 3
$C_2HCl_4 + Cl_2$ $= CHCl_2CCl_3 + Cl$	(b)	5.1 ± 0.2	11.5 ± 0.2	80–140	$CHCl{:}CCl_2/Cl_2$ P	5, 3, 12
$C_2Cl_5 + Cl_2 = C_2Cl_6 + Cl$	(a)	5.5	11.3	87–247	$CCl_2{:}CCl_2/Cl_2$ P	6, 7
$CF_2CF_2Cl + Cl_2$ $= CF_2ClCF_2Cl + Cl$	(d)	0.8		30–60	$CF_2{:}CF_2/Cl_2$ P	13
$C_2F_3Cl_2 + Cl_2 = C_2F_3Cl_3$ $+ Cl$	(e)	2.3		30–60	$CF_2{:}CFCl/Cl_2$ P	13
$CFCl_2CFCl + Cl_2$ $= CFCl_2CFCl_2 + Cl$	(f)	5.35 ± 0.3		30–70	$CFCl{:}CFCl/Cl_2$ P	14
$C_2F_4Br + HBr = C_2F_4Br_2$ $+ H$		51.2	13.07	855–1013	$H_2/O_2/C_2F_4Br_2$ S.T.	15

Ratios of Rate Constants (Halogenated Ethyl Radicals)

Reactions	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)			°*C*		
(1) $C_2H_4Br = C_2H_4 + Br$ (2) $C_2H_4Br + HBr = C_2H_5Br + Br$		14 ± 2			25–54	C_2H_4/HBr γ radiation	16, 18
(1) $C_2H_4Br = C_2H_4 + Br$ (2) $C_2H_4Br + Br_2 = C_2H_4Br_2 + Br$		6.1			60–80	C_2H_4/Br_2 P	17

Notes

(a) Data on this reaction can also be found in references 8 to 11.

(b) The reactant radical is probably $CHCl_2CCl^{2}_{2}$.

(c) The reactant radical is probably $CH_2Cl\dot{C}HCl^{2}$.

(d) Calculated assuming zero activation energy for the combination of CF_2CF_2Cl radicals.

(e) Calculated assuming zero activation energy for the combination of $C_2F_3Cl_2$ radicals.

(f) Calculated assuming zero activation energy for the combination of $CFCl_2CFCl$ radicals.

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Ratios of Rate Constants (Carbonylcarbene Radicals)

Ratios of the form (1) $CCO + C_3O_2 = \text{Polymer} + nCO$
(2) $CCO + C_nH_{2n} = C_{n+1}H_{2n} + CO$

Where C_nH_{2n} is an olefine, and $C_{n+1}H_{2n}$ is the diene and/or alkyne formed by addition of a carbon atom

Olefine	Notes	k_1/k_2	Temperature	Radical source	Reference
C_2H_4	(a)	1.4	0	C_3O_2 P	1
	(a)	1.26	0	C_3O_2 P	2
	(b)	2.79	0	C_3O_2 P	2
$CH_3CH{:}CH_2$	(a)	3.93	0	C_3O_2 P	2
	(b)	9.72	0	C_3O_2 P	2
$CH_2{:}CHCH_2CH_3$	(a)	13.14	0	C_3O_2 P	2
	(b)	38.91	0	C_3O_2 P	2
$CH_2{:}C(CH_3)_2$	(a)	14.04	0	C_3O_2 P	2
cis-$CH_3CH{:}CHCH_3$	(a)	8.03	0	C_3O_2 P	2
trans-$CH_3CH{:}CHCH_3$	(a)	14.33	0	C_3O_2 P	2
$(CH_3)_2C{:}CHCH_3$	(a)	34.38	0	C_3O_2 P	2
$(CH_3)_2C{:}C(CH_3)_2$	(a)	67.20	0	C_3O_2 P	2

Notes

(a) Photolysis at 2537 Å.
(b) Photolysis at >3100 Å.

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Metathetical Reactions of Acetyl Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		($kcal\ mole^{-1}$)	($cm^3\ mole^{-1}\ sec^{-1}$)	°C		
$I_2 + CH_3CO$ $= CH_3COI + I$		0	12.6	222–268	CH_3COI/HI T	1

Ratios of Rate Constants (Acetyl and Trifluoroacetyl Radicals)

Reaction	Notes	$E_1 - E_2$	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		($kcal\ mole^{-1}$)			°C		
(1) $CH_3CO = CH_3 + CO$ (2) $CH_3CO + HBr$ $= CH_3CHO + Br$		~ 13			100–300	CH_3COCH_3 P	2
(1) $CH_3CO = CH_3 + CO$ (2) $CH_3CO + O_2 = CH_3O + CO_2$		~ 9	− 4.68 (mole cm^{-3})			CH_3COCH_3/O_2 P	3
(1) $CH_3CO + HI = CH_3CHO + I$ (2) $CH_3CO + I_2 = CH_3COI + I$		1.5	− 0.47		222–268	CH_3COI/HI T	1
(1) $CF_3CO = CF_3 + CO$ (2) $CF_3CO + Br_2$ $= CF_3COBr + Br$	(a)	6.0	− 4.7		19–251	CF_3COCF_3/Br_2 P	4

Notes

(a) Values very doubtful.

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Ratios of Rate Constants (Ethoxy Radicals)

Reactions	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°C		
(1) $C_2H_5O + (C_2H_5)_2CO = C_2H_5OH + C_2H_4COC_2H_5$ (2) $C_2H_5O + O_2 = CH_3CHO + HO_2$				0.1 ± 0.05	35	$(C_2H_5)_2CO/O_2$ P	1
(1) $C_2H_5O + (C_2H_5)_2N_2 = C_2H_5OH + C_2H_4N_2C_2H_5$ (2) $C_2H_5O + O_2 = CH_3CHO + HO_2$				0.6 ± 0.3	118	$(C_2H_5)_2N_2/O_2$ P	2
				1.1 ± 0.4	152	$(C_2H_5)_2N_2/O_2$ P	2
(1) $C_2H_5O = CH_3 + CH_2O$ (2) $C_2H_5O + C_2H_5COOC_2H_5 = C_2H_5OH + C_5H_9O_2$		7.5 ± 1			29–195	$C_2H_5COOC_2H_5$ P	3

NOTE: For further data on ethoxy radicals see reference 4.

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1. Jolley, J. Am. Chem. Soc. **79**, 1537 (1957).
2. Cerfontain and Kutschke, J. Am. Chem. Soc. **84**, 4017 (1962).
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Metathetical Reactions of Allyl Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
cyclo-C_5H_{10}		31.8 ± 3.6		450–514	CD_3COCD_3 P	1
$C_6H_5CH_3$	(a)	14 to 17		459–592	CH_2:$CHCH_2Br$ T	2
CH_2:$CHCH_2CH(CH_3)_2$		12		450–530	CH_2:$CHCH_2CH(CH_3)_2$ T	3

Note

(a) Calculated assuming a steric factor in the range 10^{-1} to 10^{-2}.

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Metathetical Reactions of *n*-Propyl Radicals [(a)]

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	°C		
n-C_3H_7CHO		6.7	11.0	98–361	n-C_3H_7CHO P	1
n-C_3H_7CHO		10.8	11.0	191–300	n-C_3H_7CHO P	1
$(n$-$C_3H_7)_2CO$		6.5	10.4	55–161	$(n$-$C_3H_7)_2CO$ P	2
$HCOOCH_2CH_2CH_3$		7.6	10.9	74–178	CH_3COCH_3 P	3
$(n$-$C_3H_7)_2N_2$		7.9	11.3	25–291	$(n$-$C_3H_7)_2N_2$ P	4

Ratios of Rate Constants (*n*-Propyl Radicals)

Reactions	Notes	k_1/k_2	Temperature range	Radical source	Reference
			°C		
(1) n-$C_3H_7 + HI$ $= C_3H_8 + I$ (2) n-$C_3H_7 + I_2$ $= C_3H_7I + I$		0.11	290	n-C_3H_7I/HI T	5, 6
(1) n-$C_3H_7 + I_2$ $= C_3H_7I + I$ (2) n-$C_3H_7 + NO$ $= C_3H_7NO$		11	25	n-C_3H_7I/NO P	7
(1) n-$C_3H_7 + I_2$ $= C_3H_7I + I$ (2) n-$C_3H_7 + O_2$ $= C_3H_7O_2$		22	25	n-C_3H_7I/O_2 P	7

Note

(a) The rate constants are based on log k (cm^3 mole^{-1} sec^{-1}) $= 10^{13.4}$ for the combination of n-propyl radicals.

References

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Metathical Reactions of Isopropyl Radicals (a)

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
			HYDROGEN ATOM TRANSFER			
Hydrogen		*(kcal mole⁻¹)*	*(cm³ mole⁻¹ sec⁻¹)*	°C		
H_2		12.5		260–320	$CH_3CH{:}CH_2$ + H	1
Alkenes						
cyclohexadiene-1,4		6.5	11.4	75–136	$(i\text{-}C_3H_7)_2CO$ P	2
cyclohexadiene-1,3		7.1 ± 0.7	11.5 ± 0.4	42–133	$(i\text{-}C_3H_7)_2CO$ P	3
Aldehydes and Ketones						
$i\text{-}C_3H_7CHO$		9.5	10.7	283–377	$i\text{-}C_3H_7CHO$ P	4
$i\text{-}C_3H_7CHO$		6.3	10.8	117–354	$i\text{-}C_3H_7CHO$ P	4
$(i\text{-}C_3H_7)_2CO$		8.5 ± 0.1	11.1	100–400	$(i\text{-}C_3H_7)_2CO$ P	5
$[(CH_3)_2CD]_2CO$	(b)	9.3 ± 0.3	10.6	200–400	$[(CH_3)_2CD]_2CO$ P	6
$[(CH_3)_2CD]_2CO$	(b)	11.7 ± 1.1	11.3	300–400	$[(CH_3)_2CD]_2CO$ P	6
Ester						
$HCOOCH(CH_3)_2$		6.6	9.9	94–181	CH_3COCH_3 P	7
Azo-compound						
$(i\text{-}C_3H_7)_2N_2$		6.5 ± 0.5	9.9	30–120	$(i\text{-}C_3H_7)_2N_2$ P	8
		6.7 ± 0.4	10.0	35–127	$(i\text{-}C_3H_7)_2N_2$ P	9

Ratios of Rate Constants (Isopropyl Radicals)

Reactions	Notes	$E_1 - E_2$	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(kcal mole⁻¹)			°C		
(1) $i\text{-}C_3H_7 + I_2 = C_3H_7I + I$ (2) $i\text{-}C_3H_7 + NO = C_3H_7NO$				22	25	$i\text{-}C_3H_7I/NO$ P	10
(1) $i\text{-}C_3H_7 + I_2 = C_3H_7I + I$ (2) $i\text{-}C_3H_7 + O_2 = C_3H_7O_2$				~ 3	25	$i\text{-}C_3H_7I/O_2$ P	10
(1) $i\text{-}C_3H_7 + i\text{-}C_3H_7I = C_3H_6 + C_3H_8 + I$	(c)			520(3130Å)	35	$i\text{-}C_3H_7I$ P	11
(2) $i\text{-}C_3H_7 + I_2 = i\text{-}C_3H_7I + I$	(c)			170(2300Å)	35	$i\text{-}C_3H_7I$ P	11
(1) $C_3H_7 + O_2 = C_3H_6 + HO_2$ (2) $C_3H_7 + O_2 = C_3H_7O_2$	(d)	19.0	6.6		345–472	C_3H_8/O_2 T	12

Notes

(a) The rate constants are based on log *k* (cm^3 mole^{-1} sec^{-1}) $= 10^{12.9}$ for the combination of isopropyl radicals.

(b) The attacking radical is $(CH_3)_2CD$.

(c) The difference in values is due to a hot radical effect. The value at 3130 Å approximates to the correct value for thermally equilibrated isopropyl radicals.

(d) Summary of a large body of literature data. The propyl radical is probably a mixture of *n* and isopropyl.

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Perfluoropropyl Radicals

Reactants	Notes	*E*	$\log_{10}A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
		(kcal mole^{-1})	*(mole^{-1} cm^3 sec^{-1})*	°C		
H_2		12.3 ± 0.4	12.64	125–243	$(n\text{-}C_3F_7)_2CO$	1
	(a)	12.1 ± 0.2	12.86	157–319	C_3F_7CHO	2
D_2		13.8 ± 0.5	12.78		$(n\text{-}C_3F_7)_2CO$	1
	(b)	12.9 ± 0.8	12.69	85–182	$(n\text{-}C_3F_7)_2CO$	3
	(a)	14.0 ± 0.1	12.98	165–297	C_3F_7CHO	2
CH_4		9.5 ± 0.5	10.99	70–166	$(n\text{-}C_3F_7)_2CO$	3
C_2H_6	(c)	9.2 ± 0.5	12.24	87–196	$(n\text{-}C_3F_7)_2CO$	3
cyclo-C_6H_{12}		5.2 ± 0.1	11.08	25–290	$(n\text{-}C_3F_7)_2CO$	4
C_3F_7CHO	(c)	4.0 ± 0.3	10.27	28–315	C_3F_7CHO	5
		5.5 ± 0.2	10.98	165–297	C_3F_7CHO	2
CH_3COCH_3		7.2 ± 0.4	11.83	27–306	C_3F_7CHO	6
$C_3F_7COC_2H_5$		8.4 ± 0.3	11.77	80–362	$C_3F_7COC_2H_5$	7

Notes

(a) These results are less reliable than those obtained from perfluoro ketone systems.

(b) Assuming $k = 10^{10.99} \exp(-9500/RT)$ for the reaction $n-C_3F_7 + CH_4 = C_3F_7H + CH_3$.

(c) For both these compounds it seems likely that errors have been made in the determination of the activation energies, although the rate constants were probably of the correct magnitude.

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Metathetical Reactions of Halogenated Propyl Radicals

Reactions	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$CCl_3CH_2CH_2 + CCl_3Br$ $= CCl_3CH_2CH_2Br$ $+ CCl_3$		3.4	8	103–193	C_2H_4/CCl_3Br P	1
$ICH_2CH_2CH_2 + I_2$ $= ICH_2CH_2CH_2I + I$	(a)	0.5	12.5		cyclo-C_3H_6/I_2 T	2

Note

(a) Estimated from the equilibrium constant and collision theory.

References

1. Tedder and Walton, Trans. Faraday Soc. **60**, 1769 (1964).
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Ratios of Rate Constants (Isopropoxy Radicals)

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°*C*		
(1) $i\text{-}C_3H_7O = CH_3CHO + CH_3$ (2) $i\text{-}C_3H_7O + (CH_3)_2CHOOCC_2H_5 = i\text{-}C_3H_7OH + R$		<6			28	$C_2H_5COOCH(CH_3)_2$ P	1
(1) $i\text{-}C_3H_7O = CH_3CHO + CH_3$ (2) $i\text{-}C_3H_7O + NO = CH_3COCH_3 + HNO$		16			175–200	$(CH_3)_2CHONO$ T	2
(1) $i\text{-}C_3H_7O + CH_3CHO = i\text{-}C_3H_7OH + CH_3CO$ (2) $i\text{-}C_3H_7O + (i\text{-}C_3H_7O)_2 = i\text{-}C_3H_7OH + R$				27 ± 4	26	$(i\text{-}C_3H_7O)_2$ P	3

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Metathetical Reactions of Butyl Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		HYDROGEN ATOM TRANSFER				
(i) *n*-butyl radicals	(a)	(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
n-C_4H_9CHO		5.4	10.9	61–229	n-C_4H_9CHO P	1
$HCOOCH_2CH_2CH_2CH_3$		5.3	10.2	75–186	CH_3COCH_3 P	2
(ii) sec-butyl radicals	(a)					
$CH_3CH_2CH(CH_3)CHO$		4.9	10.7	25–349	$CH_3CH_2CH(CH_3)CHO$ P	3
(iii) iso-butyl radicals	(a)					
i-C_4H_9CHO		12.7 ± 0.2	12.62 ± 0.05	178–279	i-C_4H_9CHO P	4
i-C_4H_9CHO		6.5 ± 0.1	11.71 ± 0.07	117–230	i-C_4H_9CHO P	4
$(i$-$C_4H_9)_2CO$		7.6	11.4	78–194	$(i$-$C_4H_9)_2CO$ P	5
	(c)	6.8 ± 0.2	11.06 ± 0.09			4
(iv) *t*-butyl radicals	(b)					
$(CH_3)_3CCHO$		10.0	11.2	240–386	$(CH_3)_3CCHO$ P	6
$(CH_3)_3CCHO$	(d)	4.3	9.8	60–386	$(CH_3)_3CCHO$ P	6

Ratios of Rate Constants (*t*-Butyl Radical)

Reaction	Notes	$E_1 - E_2$	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°C		
(1) t-$C_4H_9 + HBr = C_4H_{10} + Br$ (2) t-$C_4H_9 + Br_2 = C_4H_9Br + Br$		8.0	5.11		40–85	$(CH_3)_3CH/Br_2$ T	7, 8, 9
(1) t-$C_4H_9 + HI = C_4H_{10} + I$ (2) t-$C_4H_9 + I_2 = C_4H_9I + I$				0.226 0.234 0.251	526 552 583	$(CH_3)_3CH/I_2$ T	8

Notes

(a) The rate constants are based on log k (cm^3 mole^{-1} sec^{-1}) $= 10^{14}$ for the combination of *n*-, *sec*-, and *iso*-butyl radicals.

(b) The rate constants are based on log k (cm^3 mole^{-1} sec^{-1}) $= 10^{12.5}$ for the combination of *t*-butyl radicals.

(c) Recalculation of data from reference 5.

(d) This value of the activation energy is probably low.

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Metathetical Reactions of *t*-Butoxy Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$(CH_3)_3CH$		4.0	10.8	25–79	D.T.B.P. P	4

Ratios of Rate Constants (*t*-Butoxy Radicals)

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°*C*		
(1) $(CH_3)_3CO+CH_2O$ $=(CH_3)_3COH+HCO$ (2) $(CH_3)_3CO$ $=CH_3+CH_3COCH_3$				(3.8 ± 0.8) $\times10^5$ cm^3 mole^{-1}	135	D.T.B.P. T	1
(1) $(CH_3)_3CO+((CH_3)_3CO)_2$ $=(CH_3)_3COH+R$ (2) $(CH_3)_3CO$ $=CH_3+CH_3COCH_3$		-3			25–79	D.T.B.P. P	2
(1) $(CH_3)_3CO+(CH_2)_2NH$ $=(CH_3)_3COH+R$ (2) $(CH_3)_3CO$ $=CH_3+CH_3COCH_3$		-12 ± 2			129–154	D.T.B.P. P	3

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Metathetical Reactions of Peracid Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
			HYDROGEN ATOM TRANSFER			
(i) Peracetic Radicals		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
CH_3CHO		$k=(8.05\pm2.40)\times10^6$		20	CH_3CHO/O_2 P	1
(ii) Perpropionic Radicals						
C_2H_5CHO		$k=(4.35\pm0.91)\times10^7$		22	C_2H_5CHO/O_2 P	1

Ratio of Rate Constants (Peracid Radicals)

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
(i) Peracetic Radicals		(*kcal mole*$^{-1}$)			°C		
(1) $CH_3CO_3+CH_3CHO$ $=CH_3CO_3H+CH_3CO$ (2) $2CH_3CO_3$ $=(CH_3CO)_2O_2+O_2$		$E_1-\frac{1}{2}E_2=7.2\pm1.0$			20–30	CH_3CHO/O_2 P	2
(ii) Perpropionic Radicals							
(1) $C_2H_5CO_3+C_2H_5CHO$ $=C_2H_5CO_3H+C_2H_5CO$ (2) $2C_2H_5CO_3$ $=(C_2H_5CO)_2O_2+O_2$		$E_1-\frac{1}{2}E_2=6.75\pm0.5$			20–47	C_2H_5CHO/O_2 P	3

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Metathetical Reactions of Peroxy Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
			HYDROGEN ATOM TRANSFER			
(i) Isobutyl peroxy radicals		*(kcal mole^{-1})*	*(cm^3 mole^{-1} sec^{-1})*	°*C*		
$(CH_3)_3CH$	(a) (b)	16.0	$4\times10^{-2}Z$	327–427	$(CH_3)_3CH/O_2 \quad -H$	1
(ii) Cyclohexenyl peroxy radicals						
cyclohexene	(a) (b)	7.0	$6\times10^{-7}Z$	152–352	$C_6H_{10}/O_2 \quad -H$	1
(iii) Isopropyl benzene peroxy radicals						
$C_6H_5CH(CH_3)_2$	(a) (b)	7.0	$2\times10^{-6}Z$	252–357	$C_6H_5CH(CH_3)_2 \quad -H$	1

Notes

(a) The peroxy radical is the radical formed by oxygen addition to any hydrocarbon radical produced in the primary act.

(b) "*Z*" is the collision number.

Reference

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Metathetical Reactions of Phenyl Radicals

Reactants	Notes	E	$\log_{10}A$ [(a)]	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
H_2		6.5	10.97	180–350	$(C_6H_5)_2Hg$ P	1
CH_4		7.5 11.1	11.19 11.9	180–350 277–407	$(C_6H_5)_2Hg$ P $CH_3COC_6H_5$ P	1 2
cyclo-C_3H_6		8.5	11.4	310–407	$CH_3COC_6H_5$ P	2
i-C_4H_{10}		6.7	11.8	277–407	$CH_3COC_6H_5$ P	2
$CH_3COC_6H_5$		6.2	11.6	277–407	$CH_3COC_6H_5$ P	2
CF_3H		5.2	10.17	180–350	$(C_6H_5)_2Hg$ P	1
GROUP TRANSFER REACTION						
$C_6H_5 + C_6H_5COCH_3$ $= C_6H_5C_6H_5 + CH_3CO$		6.2	9.6	277–407	$CH_3COC_6H_5$ P	2

Note

(a) These values are based on log k (cm^3 mole^{-1} sec^{-1}) = 10^{14} for the combination of phenyl radicals.

References

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Ratios of Rate Constants (Tolyl Radicals)

Reactions	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°C		
(1) $CH_3C_6H_4 + C_6H_4(CH_3)_2$ $= CH_3C_6H_5$ $+ CH_3C_6H_4CH_2$ (2) $CH_3C_6H_4 + D_2$ $= CH_3C_6H_4D + D$	(a)			10.7	700	$(CH_3)_2C_6H_4/D_2$ T	1
(1) *p*-$CH_3C_6H_4 + C_6H_4(CH_3)_2$ $= CH_3C_6H_5$ $+ CH_3C_6H_4CH_2$ (2) *p*-$CH_3C_6H_4 + D_2$ $= CH_3C_6H_4D + D$	(b)			24.6	484	*p*-$(CH_3)_2C_6H_4/D_2$ T	2

Notes

(a) No distinction was made between the *o*, *m*, and *p* xylenes.

(b) There appears to be a misprint in the original paper. The numbering of the reactions has been reversed.

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Hydroxyl Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
Hydrogen		*(kcal mole^{-1})*	*(cm^3 mole^{-1} sec^{-1})*	°C		
H_2		11.0	14.52	105–216	H_2O/ discharge	1
		$k=2.0\times10^{10}$		520	H_2/O_2 ignition	2
	(a)	10.0	14.1			3
		10.0	14.40		H_2O_2 flames	4
		$k=4.3\times10^{9}$		37	NO_2/H reaction	5
	(b)	5.9 ± 1.0	13.80 ± 0.7	27–1700		6
		$k=(3.5\pm0.3)\times10^{9}$		27	H_2/ discharge	7
	(b) (c)	$5.0(5.3)\pm0.6$	13.13(13.33)	27–799		8
	(b) (c)	$5.3(5.5)\pm0.6$	13.33(13.49)	27–799		9
		$k=1.1\times10^{12}$		642	H_2/O_2 flame	10
		$k=(3.9\pm0.2)\times10^{9}$		27	NO_2/H reaction	11
	(b)	5.2	13.36	27–1677		11
		6.4	14.17	687–807	H_2/O_2 ignition	12
Alkanes						
CH_4		8.3	14.38		H_2O/ discharge	13
		9.0	14.54	1027–1527	CH_4/O_2 flame	14
		$k=2\times10^{13}$		1377–1567	CH_4/O_2 flame	15
		6.5	14.15	930–1530	CH_4/O_2 flame	16
	(d)	7.9	14.36			17
C_2H_2		$k=2\times10^{12}$		1400–1700	C_2H_2/O_2 flame	18
		7.3	14.44	50–237	H_2O/ discharge	19
C_2H_4		$k=1\times10^{13}$		977–1127	C_2H_4/O_2 flame	20
		6.4	14.60	77–178	H_2O/ discharge	19
C_2H_6		5.5	14.11	65–228	H_2O/ discharge	19
		$k=2.5\times10^{13}$		1147–1337	$C_2H_6/H_2/O_2$ flame	34
	(e)	$k=2.1\times10^{13}$		520	H_2/O_2 ignition	21
		$k=5\times10^{12}$		1027–1227	C_2H_6/O_2 flame	20
C_3H_8	(e)	$k=4.3\times10^{13}$		520	H_2/O_2 ignition	21
n-C_4H_{10}		$k=5.8\times10^{13}$		520	H_2/O_2 ignition	21
i-C_4H_{10}		$k=3.2\times10^{13}$		520	H_2/O_2 ignition	21
Aldehydes						
HCHO		0.9	14.11	73–216	H_2O/ discharge	22
	(b)	13.0	15.7	73–1339		20
CH_3CHO		4.0	13.53	53–209	H_2O/ discharge	22
Acid						
HNO_3		$k=1.0\times10^{11}$		27	HNO_3 flash photolysis	23
Halogenated Alkane						
CH_3Br		$k=1.5\times10^{13}$		1527–1727	CH_4/O_2 flame	24

Hydroxyl Radicals—Continued

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		(kcal mole⁻¹)	*(cm³ mole⁻¹ sec⁻¹)*	°C		
OXYGEN ATOM TRANSFER						
CO	(g)	7.0	13.08	70–203	H_2O/ discharge	1
	(a)	5.7	12.46			3
		$k=9\times10^{11}$		1677	CH_4/O_2 flame	15
	(d)	5.7	12.46			17
	(b)	7.7	12.85	127–1727		20
		4.0	12	1107–1447	flame study.	25
	(b)	6.2 ± 0.6	12.6 ± 0.3	107–1677		8
	(b) (c)	$0.5(0.8)\pm0.6$	$11.5(11.7)\pm0.3$	200–800		8
		$k=(1.15\pm0.5)\times10^{11}$		27	NO_2/H reaction	11
	(b)	0.6	11.49	27–1677		11
MISCELLANEOUS REACTIONS						
$OH+F_2=HF+F+O$		18.0	15.3		F_2/H_2O flames	26
		18.0	13.85	497–557	F_2/H_2O ignition	26

Hydroxyl Radicals (Rate Constant Ratios)

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(kcal mole⁻¹)			°C		
(1) $C_2H_6+OH=C_2H_5+H_2O$ (2) $H_2+OH=H+H_2O$	(f)			12	540	H_2/O_2 ignigion	27
(1) $C_3H_8+OH=C_3H_7+H_2O$ (2) $H_2+OH=H+H_2O$	(f)			27	520	H_2/O_2 ignition	27
(1) n-$C_4H_{10}+OH=C_4H_9+H_2O$ (2) $H_2+OH=H+H_2O$	(f)			36	520	H_2/O_2 ignition	27
(1) i-$C_4H_{10}+OH=C_4H_9+H_2O$ (2) $H_2+OH=H+H_2O$	(f)			20	520	H_2/O_2 ignition	27
(1) $HCHO+OH=HCO+H_2O$ (2) $H_2+OH=H+H_2O$	(f)			42	540	H_2/O_2 ignition	27
(1) $(C_2H_5)_4Si+OH$ $=(C_2H_5)_3Si.C_2H_4+H_2O$ (2) $H_2+OH=H+H_2O$	(f)			74	520	H_2/O_2 ignition	27
(1) $H_2O_2+OH=HO_2+H_2O$ (2) $H_2+OH=H_2O+H$				4.8 to 5.7	447	H_2/O_2 ignition	28
				7.1	500	H_2/O_2 ignition	29
				5.5	440	H_2/O_2 ignition	30
				4.3 ± 0.3	440	H_2/O_2 pyrolysis	27
				4.7	500	H_2 combustion	27

Hydroxyl Radicals (Rate Constant Ratios)—Continued

Reaction	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(kcal mole⁻¹)			°C		
(1) $H_2+OH=H+H_2O$ (2) $CO+OH=CO_2+H$		4.0 ± 0.3	1.49 ± 0.7		200–350	H_2O photolysis	31
				5.0	520	H_2/O_2 ignition	27
				3.3		CO/H_2 combustion	27
	(b)	5.16	1.98		500–1002		27
	(b)	4.6 ± 0.3	1.87		27–1002		11
(1) $D_2+OH=D+HDO$ (2) $CO+OH=CO_2+H$		6.4 ± 0.3	2.20 ± 0.09		200–300	H_2O photolysis	31
(1) $CH_4+OH=CH_3+H_2O$ (2) $CO+OH=CO_2+H$		7.3	2.28		400–650	H_2O_2 pyrolysis	32
(1) $HCHO+OH=HCO+H_2O$ (2) $CH_4+OH=CH_3+H_2O$				33	525	H_2O_2 pyrolysis	32
				27	600	H_2O_2 pyrolysis	32
				22	650	H_2O_2 pyrolysis	32
				33	500	CH_4 combustion	33

Notes

(a) Used at flame temperatures.

(b) Critical survey of literature data.

(c) ΔH_f (OH) = 9.33 (10.0) kcal/mole.

(d) This value was used by the authors in the region 1000°–1500° but its origin was not stated.

(e) Measured relative to $OH+H_2=H_2O+H$, for which $k=1.6\times10^9$ at 520 °C.

(f) Calculated on the assumption that oxygen atom reactions could be neglected.

(g) The products of this reaction are CO_2+H.

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Metathetical Reactions of Hydroperoxyl Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
			HYDROGEN ATOM TRANSFER			
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
H_2		24.0	11.08		H_2/O_2 ignition	1, 2
		$k=1.1\times10^7$		500	H_2/O_2 ignition	3
		14.8 ± 2.2		617–1007	H_2/O_2 ignition	4
		$k=1.3\times10^6$		500		7
		34.6	16.51	687–807		9
H_2O	(a)	8.0	8.1	600–615	H_2/O_2 ignition	1, 8
	(b)	30.0	13.26	600–615	H_2/O_2 ignition	2

Ratios of Rate Constants (Hydroperoxyl Radicals)

Reactions	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°*C*		
(1) $CO+HO_2=CO_2+OH$ (2) $H_2+HO_2=H+H_2O_2$				9.5 ± 2	500	$H_2/CO/O_2$ ignition	5
(1) $HCHO+HO_2$ $=HCO+H_2O_2$ (2) $CO+HO_2=CO_2+OH$				340	525	CH_4/O_2 T	6

Notes

(a) These values must be rejected on thermochemical grounds.
(b) Is a recalculation of data from (a).

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Metathetical Reactions of Imino Radicals

Reactants	Notes		E	$\log_{10}A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER							
			($kcal\ mole^{-1}$)	($cm^3\ mole^{-1}\ sec^{-1}$)	°C		
HNCO	(a)	3.6			−31–200	HNCO P	1

Note

(a) The products of this reaction are NH_2 and NCO.

Reference

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Metathetical Reactions of Amino Radicals

Reactants	Notes	E	$\log_{10}A$	Temperature range	Radical source	References
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$NH_2+N_2H_4$ $=NH_3+N_2H_3$		$k=7.9\times10^{10}$		25		1
		17	13.5	830–1130	N_2H_4 S.T.	4
$NH_2+O_2=NH+HO_2$		42.5 ± 1.2		1277–2027	NH_3/O_2 S.T.	2

Metathetical Reactions of Amino Radicals Ratios of Rate Constants

Reactants	Notes	E_1-E_2	$\log_{10}A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°*C*		
(1) $NH_2+(CH_3)_2N\cdot NH_2$ $=NH_3+(CH_3)_2N\cdot NH$ (2) $NH_2+(CH_3)_2N\cdot NH_2$ $=NH_3+(CH_3)(CH_2)N\cdot NH_2$				6.6×10^{-3}	250	$(CH_3)_2N.NH_2$ T	3

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Metathetical Reactions of Difluoroamino Radicals

Reactions	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER						
Alkanes		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
n-C_4H_{10}		22.20 ± 0.08	11.83 ± 0.04	180–282	N_2F_4/n-C_4H_{10} T	1
i-C_4H_{10}		18.49 ± 0.10	10.49 ± 0.04	155–282	N_2F_4/i-C_4H_{10} T	1
cyclo-C_5H_{10}		19.91 ± 0.11	10.93 ± 0.05	180–282	N_2F_4/cyclo-C_5H_{10} T	1
neo-C_5H_{12}		26.68 ± 0.07	13.22 ± 0.03	180–282	N_2F_4/neo-C_5H_{12} T	1
Ketone						
CH_3COCH_3		19.56 ± 0.11	10.71 ± 0.05	170–280	N_2F_4/CH_3COCH_3 T	2
FLUORINE ATOM TRANSFER						
F_2O		22.5 ± 0.7	14.01	120–170	N_2F_4/F_2O T	3

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Metathetical Reactions of Nitrate Radicals

Reactions	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
$NO_3 + NO = 2NO_2$		$k = 6 \times 10^{12}$		27		1
		1.4 ± 2.5	13.8		N_2O_5 S.T.	2
		$k = 2.7 \times 10^{12}$		27	NO_2/O_3 P	3
		1.7	12.62	200–550	NO_2 T	4
		$k = 1 \times 10^{14}$		25	NO_2 F.P.	5
$NO_3 + NO_2 = NO_2 + NO + O_2$		3.9 ± 1.0	11.22	27–547	N_2O_5 S.T.	1, 2
		3.2 ± 1.0	11.07 ± 0.47	200–550	NO_2 T	4
$NO_3 + NOCl = NO_2 + NO_2Cl$	(a)	$k = 7.0 \times 10^7$		40	$NOCl/O_3/N_2O_5$ T	6
		$k = 2.3 \times 10^7$		40		2

Ratios of Rate Constants

Reactions	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°C		
(1) $NO_3 + NO = 2NO_2$ (2) $NO_3 + NO_2 = NO_2 + NO + O_2$				60	434	NO_2 T	7
	(b)	1.4	2.2		20–30	NO/N_2O_5 T	8, 9
	(c)	2.3	3.2		20–30	NO/N_2O_5 T	8, 9

Notes

(a) The A factor was assumed, only the rate constant was determined.
(b) At 400 mm total pressure.
(c) At 57 mm total pressure.

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Metathetical Reactions of Thiyl Radicals

Reactant	Note	E	$\log_{10} A$	Temperature range	Radical source		References
HYDROGEN ATOM TRANSFER							
		(kcal mole^{-1})	*(cm^3 mole^{-1} sec^{-1})*	*°C*			
CH_3OCH_3	(a)	6.8	11	360–440	CH_3OCH_3/H_2S	T	1, 2

Notes

(a) For further data on systems containing HS radicals, see reference 3.

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Reactions of Chloromonoxy Radicals

Reactions	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$ClO + Cl_2O = ClO_2 + Cl_2$		$k = 10^8$			Cl_2O F.P.	1
$ClO + Cl_2O = Cl + O_2 + Cl_2$		$k = 5.3 \times 10^7$			Cl_2O F.P.	1
$ClO + NO_3Cl = NO_2 + Cl_2 + O_2$		~ 17		90–130	NO_3Cl T	2

Ratios of Rate Constants (Chloromonoxy Radicals)

Reactions	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°*C*		
(1) $ClO + C_3H_8 = HOCl + CH_3CHCH_3$ (2) $ClO + C_3H_8 = HOCl + CH_3CH_2CH_2$				7.2 ± 0.5	100	C_3H_8/Cl_2O T	3

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Reactions of Borine Radicals

Reactants	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
$BH_3 + B_2H_6 = B_3H_7 + H_2$		11.5	11.06			1, 9
$BH_3 + B_2D_6 = BH_3BD_3 + BD_3$		6.0 7.8	14.2 13.45	24–44	B_2H_6/B_2D_6. T	4, 5, 6, 3 1
$BH_3 + BH_3CO = B_2H_6 + CO$		7.0	11.4	0–30	BH_3CO T	7, 4, 3
$BH_3 + H_2O = BH_2OH + H_2$		6	11.28	51	B_2H_6/H_2O T	8, 9
$BH_3 + HD = BH_2D + H_2$		7	11.6			9

Ratios of Rate Constants Involving Borine Radicals

Reaction	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°C		
(1) $BH_3 + B_2D_6 = BD_3BH_3 + BD_3$ (2) $BH_3 + D_2 = BH_2D + HD$				0.25	55	B_2H_6/D_2 T	2, 3
(1) $BH_3 + O_2 = BH_2OH + O$ (2) $BH_3 + O_2 + M = HBO_2 + H_2 + M$		2.0			150–200	B_2H_6/O_2 T	1

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Metathetical Reactions of F_3SO and FSO_3 Radicals

Reactions	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		($kcal\ mole^{-1}$)	($cm^3\ mole^{-1}\ sec^{-1}$)	°C		
$F_3SO + F_2 = F_4SO + F$		10.0 ± 2		5–20	F_2/F_2SO P	1
$FSO_3 + F_2 = F_2SO_3 + F$		14.7 ± 1.0	8.68	230–250	$F_2/F_2S_2O_6$ T	2

References

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Radical Disproportionation Reactions

The reactions are classified in the same order as the tables of radical reactions. Thus the first set of reactions are those involving atoms, followed by reactions of radicals containing one carbon atom, etc.

Reactions	Notes	E	$\log_{10} A$	$\log_{10} k$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$H + OH = H_2 + O$		5.8 ± 1.5	12.76 ± 1.0		25–2000		4
		7.4	12.74		687–807	H_2/O_2 S.T.	12
$H + HO_2 = 2OH$				14.86	25	H_2/O_2 −H	5
				13.84	500		6
$H + HNO = H_2 + NO$				> 9.78	20	H_2/discharge	1
				> 10.48	−47	H_2/discharge	2
				12.78 ± 0.25	1300–1700	$H_2/O_2/N_2$ flame	3
$H + C_2F_4Br = C_2F_4 + HBr$		11.5	16.3		855–1013	$H_2/O_2/C_2F_4Br_2$ S.T.	7
$Cl + C_2HCl_4 = C_2HCl_3 + Cl_2$				13.85	224	$CHCl{:}CCl_2/Cl_2$ P	25, 24
$Cl + C_2Cl_5 = C_2Cl_4 + Cl_2$		1.2	15.6				24
$Cl + COCl = CO + Cl_2$		0.8	14.6		25–55	CO/Cl_2 P	33, 24
	(a)	2.4	13.70		15–450		34
$Cl + Cl_3 = 2Cl_2$				$\leqslant 14.23$	20	Cl_2/discharge	19, 20
$I + NOI = NO + I_2$				12.60	60	NO/I_2 F.P.	30
$2CN = C_2 + N_2$		96			3177–4527	C_2N_2 S.T.	14, 15
$2C_2H_3Cl_2 = C_2H_3Cl + C_2H_3Cl_3$		0.3	12.9		25–55	$CH_2{:}CHCl/Cl_2$ P	29
$2CHCl_2CHCl = CHCl{:}CHCl + CHCl_2CHCl_2$		0.5 ± 0.5	13.47 ± 0.3		30–65	*cis*-$CHCl{:}CHCl/Cl_2$ P	31
$2C_2Cl_5 = C_2Cl_4 + C_2Cl_6$		0.08	11.66		87–247	C_2Cl_4/Cl_2 P	32
$2CH_3CO_3 = (CH_3CO)_2O_2 + O_2$				13.95	20	CH_3CHO/O_2 P	27
$2C_2H_5CO_3 = (C_2H_5CO)_2O_2 + O_2$				13.43	22	CH_3CH_2CHO/O_2 P	28
$2OH = H_2 + O_2$		48.6	12.85		687–807	H_2/O_2 S.T.	12
$2OH = H_2O + O$				12.18	37–107	H_2/discharge	10
	(b)			12.08	27	H_2/discharge	11
		1.0 ± 0.5	12.88 ± 0.3		25–2000		4
		3.8	14.87		687–807	H_2/O_2 S.T.	12
	(b)			12.19	27	NO_2/H reaction	13
$OH + HNO = H_2O + NO$ (or $H_2 + NO_2$)				13.95	1300–1700	$H_2/O_2/NO$ flame	3
$2HO_2 = H_2O_2 + O_2$				12.25	room temp.		6
				13.81	25	H_2/O_2 −H	5
$2NH_2 = NH_3 + NH$				13.40	1627–2127	NH_2NH_2 S.T.	8
				11.66		NH_3 F.P.	9
$2N_2H_3 = 2NH_3 + N_2$				$\geqslant 12.48$	150	H_2/discharge	18

Radical Disproportionation Reactions—Continued

The reactions are classified in the same order as the tables of radical reactions. Thus the first set of reactions are those involving atoms, followed by reactions of radicals containing one carbon atom, etc.

Reactions	Notes	E	$\log_{10} A$	$\log_{10} k$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$2HNO = H_2O + N_2O$				> 7.48	27	NO/H reaction	16
				~ 8.9	190	$(CH_3)_2CHNO$ T	17
$2NO_3 = 2NO_2 + O_2$		7.7 ± 1.0	12.42		280–830	N_2O_5 S.T.	26
$2ClO = Cl_2 + O_2$				10.38		Cl_2O F.P.	21
				10.93	20	Cl_2O F.P.	22, 23

Ratios of Rate Constants (Radical Disproportion Reactions)

Reactions	Notes	Rate constants ratios	Temperature range	Radical source	Reference
		cm^3, *mole. sec. units*	°*C*		
(1) $H + HO_2 = 2OH$ (2) $2HO_2 = H_2O_2 + O_2$		$k_1^2/k_2 = 5.1 \times 10^{14}$	500	H_2/O_2 ignition	35, 36
(1) $2HS = H_2 + S_2$ (2) $2HS = H_2S + S$		$k_1/k_2 = 0.15$	room temp.	H_2S P	37
(1) $2HNO = H_2O + N_2O$ (2) $2HNO = 2NO + H_2$		$k_1/k_2 = 8$	25	C_2H_5OH/NO H	38
(1) $C_2H_5 + C_5H_9O_2 = C_2H_4 + C_2H_5COOC_2H_5$ (2) $C_2H_5 + C_5H_9O_2 = C_2H_6 + C_5H_8O_2$		$k_1/k_2 = 0.1$	29	$C_2H_5COOC_2H_5$ P	39
(1) $2C_2H_5O = C_2H_5OH + CH_3CHO$ (2) $C_2H_5O = CH_3 + CH_2O$		$k_1/k_2^2 = 1.2 \times 10^{10}$ $k_1/k_2^2 = (3 \pm 1) \times 10^{12}$	152 30	$C_2H_5COOC_2H_5$ P $C_2H_5COOC_2H_5$ P	40 40
(1) $2(CH_3)_3CO = (CH_3)_3COH + (CH_3)_2\overline{CCH_2O}$ (2) $(CH_3)_3CO = CH_3COCH_3 + CH_3$		$k_1/k_2^2 \leq 3.0 \times 10^8$	25	$((CH_3)_3CO)_2$ P	41

Notes

(a) Review of literature data.

(b) Value based on E.S.R. measurements of the radical concentration.

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Disproportionation/Combination Ratios

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(a) Hydrogen Atom Transfer

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Reactions of

(b) Chlorine Atom Transfer

(c) Oxygen Atom Transfer

Disproportionation/Combination Ratios

The following convention is used throughout this table, e.g. for ethyl and *n*-propyl radicals, the possible reactions are:

$$C_2H_5 + n\text{-}C_3H_7 = C_5H_{12} \qquad (1)$$

$$C_2H_5 + n\text{-}C_3H_7 = C_2H_6 + C_3H_6 \qquad (2)$$

$$C_2H_5 + n\text{-}C_3H_7 = C_2H_4 + C_3H_8 \qquad (3)$$

k_2/k_1 is listed as $C_2H_5/n\text{-}C_3H_7$ and k_3/k_1 as $n\text{-}C_3H_7/C_2H_5$.

The table is constructed with reference to the radical receiving the transferred atom. In the above example, k_2/k_1 is in the section on ethyl radicals and k_3/k_1, with the *n*-propyl radicals. The radicals are further classified according to the number of carbon atoms they contain. Thus the table starts with H atom reactions, followed by C_1 reactions (methyl radicals and halogen and oxygen containing derivatives of methyl radicals,) then by C_2 reactions, etc.

Reactants	Notes	*k*dis/*k*comb.	Temperature range	Radical source	Reference
HYDROGEN ATOM TRANSFER					
Hydrogen atom			°C		
H/C_2H_5		0.05 ± 0.03	26–203	$(C_2H_5)_2CO + H_2$ −H	1
D/C_2H_5	(a)	0.21 ± 0.07	26–203	$(C_2H_5)_2CO + D_2$ −H	1
D/CH_3CD_2		0.06 ± 0.03	26–203	$(CH_3CD_2)_2CO + D_2$ −H	1
$D/i\text{-}C_3H_7$		0.2	85		2
H/C_5H_{11}		0.099	25	iso-C_5H_{12} −H	3
H/C_6H_{13}		0.12	25	$n\text{-}C_6H_{14}$ −H	4
Methyl					
$CH_3/CH_2{:}CH$		2.3	175	$CH_2{:}CHCHO$ and $HCOOCH{:}CH_2$ $+ CH_3$	5
CH_3/C_2H_5		0.04 ± 0.02	78–130	$CH_3COC_2H_5$ P	6
		0.055	77–230	$HCOOC_2H_5 + CH_3$	7
		0.039 ± 0.007	110–166	$(CH_3)_2CO + (C_2H_5)_2CO$ P	8
		0.039			
CH_3/CH_3CD_2		0.06 ± 0.01	90	$(CH_3)_2CO$ $+ (CH_3CD_2)_2CO$ P	9
CD_3/C_2H_5		< 0.08	27	$(CD_3)_2CO + (C_2H_5)_2CO$ P	10
$CH_3/n\text{-}C_3H_7$		0.095 ± 0.01	74–178	$HCOOCH_2CH_2CH_3$ $+ CH_3$	11
		0.025 ± 0.004	139–173	$n\text{-}C_3H_7CHO$ $+ CH_3$	12
		0.041 ± 0.01	118–144	$(CH_3)_2CO$ $+ (n\text{-}C_3H_7)_2N_2$ P	8
	(b)	0.14			13

Disproportionation/Combination Ratios—Continued

Reactants	Notes	*k*dis/*k*comb.	Temperature range	Radical source	Reference
			°C		
$CD_3/CH_3CH_2CD_2$		0.05	25–28	$CD_3COCD_2CH_2CH_3$ P	14
$CH_3/i\text{-}C_3H_7$		0.216 ± 0.032	80–150	$(CH_3)_2CO + CH_3COCH(CH_3)_2$ P	15
		0.195 0.21	94–181	$HCOOCH(CH_3)_2 + CH_3$	11
CD_3/CH_3CDCH_3		0.17 ± 0.03	53–116	$CD_3COCD(CH_3)_2$ P	16
$CH_3/n\text{-}C_4H_9$		0.15	70–195	$HCOOC_4H_9 + CH_3$	13, 103
$CH_3/sec\text{-}C_4H_9$		0.30	−103–+25	*cis*-$CH_3CH{:}CHCH_3 + H$	17
		0.07	107–168	$CH_3CH{:}CH_2 + CH_3$	18
$CH_3/t\text{-}C_4H_9$	(c)	0.85 ± 0.1	20–60	$((CH_3)_3CO)_2$ P	19
		0.88	25–79	$((CH_3)_3CO)_2$ P	20
		0.699 ± 0.037	80–188	$((CH_3)_3C)_2CO$ P	15
	(d)	0.806 0.80			21
$CH_3/n\text{-}C_5H_{11}$		0.1	63	$CH_3COC_5H_{11}$ P	22
$CD_3/cyclo\text{-}C_5H_9$		0.31	132–218	$(CD_3)_2CO$ P	23
CH_3/CDO		2.5	80–180	$(CH_3)_2N_2$ P	24
CH_3/CH_3O		1.25	29	CH_3COOCH_3 P	25
	(a)	1.51 ± 0.2	124–185	CH_3OOCH_3 T	26
CH_3/CD_3O		1.4 ± 0.1	30–201	CH_3COOCD_3 P	27
CD_3/CD_3O		1.8	30–201	CH_3COOCD_3 P	27
CH_3/CH_3CO		0.06	29	CH_3COOCH_3 P	25
		0.05	30	CH_3COOCD_3 P	104
		$\leqslant 0.095$	55	$CH_3CO.COCH_3$ −H	28
CD_3/CD_3CO		0.014 to 0.055	25	$CD_3COCD_2CH_2CH_3$ P	14
CH_3/CH_3COCH_2		0.25 ± 0.25	184–285	CH_3COCH_3 P	29
$CH_3/(CH_3)_2CHO$		3.4	26	$((CH_3)_2CHO)_2$ P	30
Methoxy					
CH_3O/CH_3O		$\geqslant 60$	25	$(CH_3)_2N_2 + O_2$ P	31
		9.3 ± 0.6	room temp.	$CH_3I + O_2$ P	32
Halogenated Methyls					
CCl_3/C_2H_5		0.24 ± 0.04	25	$(C_2H_5)_2CO + CCl_4$ P	33
		0.22 ± 0.03	0–58	$C_2H_4 + CCl_4$ P	34
CCl_3/C_2H_4Cl		0.11 ± 0.02	26	$C_2H_4 + CCl_4$ P	105
		0.14 ± 0.03	0–58	$C_2H_4 + CCl_4$ P	34
$CCl_3/C_2H_4COC_2H_5$		0.9 ± 0.1	25	$(C_2H_5)_2CO + CCl_4$ P	33

Disproportionation/Combination Ratios—Continued

Reactants	Notes	*k*dis/*k*comb.	Temperature range	Radical source	Reference
			°C		
CF_2H/CF_2H		0.19	75–119	CF_2ClH − H	35
Vinyl					
$CH_2{:}CH/CH_2{:}CH$		1.1	175	$CH_2{:}CHCHO$ and $HCOOCH{:}CH_2$ + CH_3	5
	(e)	0.5	272–301		5
		0.02	50	$(CH_2{:}CH)_2Hg$ P	36
$CH_2{:}CH/C_2H_5$		0.03	161–175	$(C_2H_5)_2CO$ P	37
Ethyl					
$C_2H_5/CH_2{:}CH$		0.12	161–175	$(C_2H_5)_2CO$ P	37
C_2H_5/C_2H_5		0.36	75	$(C_2H_5)_2Hg$ P	38
		0.46	200	$(C_2H_5)_2Hg$ P	38
		0.11	25	$(C_2H_5)_2CO$ P	39
		0.085	101	$(C_2H_5)_2CO$ P	39
		0.17	25	C_2H_4 + H	40
		0.22–0.61	42	C_2H_4 + H	41
		0.47	200	C_2H_4 + H	41
		0.10	25	C_2H_5CHO P	42
		0.13	350	$(C_2H_5)_2Hg$ T	43
		0.13	122	C_2H_5CHO + CH_3	44
		0.15	156	C_2H_5CHO + CH_3	44
		0.13 ± 0.02	26–74	$(C_2H_5)_2N_2$ P	45
		0.12	100–200	$(C_2H_5)_2CO$ P	46
		0.15 ± 0.01	25	C_2H_4 + H	47
		0.136 ± 0.02	50–215	$(C_2H_5)_2CO$ P	48
		0.12 ± 0.01	27–118	$(C_2H_5)_2N_2$ P	49
		0.15	50–315	C_2H_5CHO P	50
		0.14	77–230	$HCOOC_2H_5$ + CH_3	7
	(f)	0.16 0.13 0.11_9	−65 0 40	$(C_2H_5)_2N_2$ P	51, 52
		0.130 ± 0.007	115–150	$(C_2H_5)_2CO$ P	8
		0.11 ± 0.01	22	$(C_2H_5)_2N_2$ F.P.	53
		0.123 ± 0.008	25–200	$(C_2H_5)_2CO$ P	54
		0.134 ± 0.003	79–141	$(C_2H_5)_2CO$ P	55
		0.11	room temp.	$CH_2{:}CH_2$ + H	56
		0.137	71–175	$(C_2H_5)_2CO$ P	106
		0.135			
CH_3CD_2/CH_3CD_2	(g)	0.1	24–180	$(CH_3CD_2)_2CO$ P	57
C_2D_5/C_2D_5		$0.098_5 \pm 0.008$	50–197	$(C_2D_5)_2CO$ P	58
C_2H_5/CH_2CHCH_2		0.05	134–175	$(C_2H_5)_2CO$ P	106
$C_2H_5/n\text{-}C_3H_7$		0.14	117	$(C_2H_5)_2CO$ + $HCOOnC_3H_7$ P	59
		0.081 ± 0.01	61–129	$(C_2H_5)_2CO$ + $(n\text{-}C_3H_7)_2N_2$ P	8
		0.06 ± 0.04	−78–+24	C_3H_8 − H	60
		0.08			

Disproportionation/Combination Ratios—Continued

Reactants	Notes	*k*dis/*k*comb.	Temperature Range	Radical Source	Reference
			°*C*		
$C_2H_5/i\text{-}C_3H_7$		0.2	room temp.	$CH_2{:}CH_2$ $+CH_3CH{:}CH_2$ +H	107
		0.21 ± 0.02	25	C_3H_8 −H	61
		0.43 ± 0.03	34–144	$HCOO\,i\text{-}C_3H_7$ $+(C_2H_5)_2CO$ P	59
		0.43	48–112	C_2H_5CHO $+i\text{-}C_3H_7CHO$ P	62
		0.43			
$C_2H_5/\text{sec-}C_4H_9$		0.23 ± 0.01	25	$n\text{-}C_4H_{10}$ −H	61
$C_2H_5/i\text{-}C_4H_9$		0.02 ± 0.02	0	$i\text{-}C_4H_{10}$ −H	60
$C_2H_5/t\text{-}C_4H_9$		0.3	room temp.	$CH_2{:}CH_2$ $+(CH_3)_2C{:}CH_2$ +H	107
		0.53	73–80	$(C_2H_5)_2CO$ $+((CH_3)_3C)_2CO$ P	62
		0.54 ± 0.01	25	$i\text{-}C_4H_{10}$ −H	61
		0.54			
$C_2H_5/\text{cyclo-}C_5H_9$		0.27 ± 0.05	25	$\text{cyclo-}C_5H_{10}$ −H	61
$C_2H_5/n\text{-}C_5H_{11}$		0.08 ± 0.04	0	$n\text{-}C_5H_{12}$ −H	60
$C_2H_5/\text{sec-}C_5H_{11}$	(h)	0.25 ± 0.01	25	$n\text{-}C_5H_{12}$ −H	61
$C_2H_5/t\text{-}C_5H_{11}$		0.60 ± 0.01	25	$(CH_3)_2CHCH_2CH_3$ −H	61
$C_2H_5/\text{cyclo-}C_6H_7$	(i)	0.38 ± 0.03	50–120	$(C_2H_5)_2CO$ P	64
$C_2H_5/(CH_3)_3CCHCH_3$		0.20 ± 0.02	25	$(CH_3)_3CCH_2CH_3$ −H	61
C_2H_5/sec-hexyl	(j)	0.27 ± 0.01	25	$n\text{-}C_6H_{14}$ −H	61
$C_2H_5/(CH_3)_2CC_3H_7$		0.74 ± 0.03	25	$(CH_3)_3CHCH_2CH_2CH_3$ −H	61
$C_2H_5/(CH_3)_2CCH(CH_3)_2$		0.72 ± 0.01	25	$(CH_3)_2CHCH(CH_3)_2$ −H	61
$C_2H_5/CH_3C(C_2H_5)_2$		0.8	25	$CH_3CH(C_2H_5)_2$ −H	61
C_2H_5/CH_3CH_2O		1.3 ± 0.2	15–29	$C_2H_5COOC_2H_5$ P	65
Ethoxy					
CH_3CH_2O/C_2H_5		2.3 ± 0.3	29	$C_2H_5COOC_2H_5$ P	65
CH_3CH_2O/CH_3CH_2O		12 ± 2	25	$C_2H_5I+O_2$ P	66
Hydroxy ethyl					
$CH_3CH(OH)/CH_3CH(OH)$	(k)	0.3	25	C_2H_5OH −H	67
Halogenated ethyl					
C_2F_5/C_2H_5		0.56	21–240	$C_2F_5COC_2H_5$ P	112
C_2H_4Cl/C_2H_5		0.22	0–58	$C_2H_4+CCl_4$ P	34

Disproportionation/Combination Ratios—Continued

Reactants	Notes	*k*dis/*k*comb.	Temperature Range	Radical Source	Reference
			°C		
C_2H_4Cl/C_2H_4Cl		≤ 0.05	0–58	$C_2H_4 + CCl_4$ P	34
		≤ 0.1	26	$C_2H_4 + CCl_4$ P	105
	(l)	0.36	23	$C_2H_4 + COCl_2$ P	68
	(m)	24	23	$C_2H_4 + COCl_2$ P	68
C_2H_4Cl/C_4H_8Cl	(n)	0.40	23	$C_2H_4 + COCl_2$ P	68
Allyl					
CH_2CHCH_2/C_2H_5		0.13	134–175	$(C_2H_5)_2CO$ P	106
***n*-Propyl**					
$n\text{-}C_3H_7/C_2H_5$		0.058 ± 0.01	61–129	$(C_2H_5)_2CO + (n\text{-}C_3H_7)_2N_2$ P	8
$n\text{-}C_3H_7/n\text{-}C_3H_7$		0.21	113	$(n\text{-}C_3H_7)_2CO$ P	69
		0.1	25	$n\text{-}C_3H_7CHO$ P	75
		0.3	30–108	$(n\text{-}C_3H_7)_2Hg$ P	63
		0.125 ± 0.01	100–150	$(n\text{-}C_3H_7)_2CO$ P	108
		0.16	25–191	$n\text{-}C_3H_7CHO$ P	70
		0.157	25–130	$(n\text{-}C_3H_7)_2N_2$ P	71
		0.14	74–178	$HCOOCH_2CH_2CH_3 + CH_3$	11
		0.141 ± 0.015	18–150	$(n\text{-}C_3H_7)_2N_2$ P	8
		0.14			
$C_2H_5CD_2/C_2H_5CD_2$		0.15	25–28	$CH_3CH_2CD_2COCD_3$ P	14
Iso-Propyl					
iso-C_3H_7/C_2H_5		0.19	48–112	$C_2H_5CHO + i\text{-}C_3H_7CHO$ P	62
		0.2	room temp.	$CH_2{:}CH_2 + CH_3CH{:}CH_2$ + H	107
		0.07	34–144	$(C_2H_5)_2CO$ P	59
		0.19			
iso-C_3H_7/iso-C_3H_7		1.5	30	$CH_3CH{:}CH_2$ + H	72
		2.	200	$CH_3CH{:}CH_2$ + H	72
		1.	270	$(i\text{-}C_3H_7)_2Hg$ T	73
		0.53	30	$(i\text{-}C_3H_7)_2N_2$ P	74
		0.5	25	$i\text{-}C_3H_7CHO$ P	75
		0.77	25	$CH_3CH{:}CH_2$ + H	76
		0.48	320	$CH_3CH{:}CH_2$ + H	76
		0.6	200	$(i\text{-}C_3H_7)_2CO$ P	77
		0.65	20–261	$i\text{-}C_3H_7CHO$ P	109
		0.5 ± 0.05	room temp.	$CH_3CH{:}CH_2$ + H	56
		0.54	61–127	$((CH_3)_2CH)_2N_2$ P	78
		0.65	94–181	$HCOO\,i\text{-}C_3H_7 + CH_3$	11
		0.58 ± 0.04	75–136	$((CH_3)_2CH)_2CO$ P	79
		0.65			
$(CH_3)_2CD/(CH_3)_2CD$		0.63 ± 0.04	25–125	$((CH_3)_2CD)_2CO$ P	80
		0.67	53–116	$(CH_3)_2CDCOCD_3$ P	16
iso-C_3H_7/sec-C_4H_9		0.4	room temp.	$CH_3CH{:}CH_2 + CH_3CH{:}CHCH_3$ + H	107

Disproportionation/Combination Ratios—Continued

Reactants	Notes	*k*dis/*k*comb.	Temperature Range	Radical Source	Reference
			°C		
iso-C_3H_7/t-C_4H_9		0.5	room temp.	$CH_3CH{:}CH_2 + (CH_3)_2C{:}CH_2 + H$	107
		0.70	72–82	$(t\text{-}C_4H_9)_2CO + (i\text{-}C_3H_7)_2CO$ P	62
iso-C_3H_7/cyclo-C_6H_7	(i)	0.52 ± 0.09	75–136	$(i\text{-}C_3H_7)_2CO$ P	79
Propoxy					
C_2H_5CO/C_2H_5		0.4 ± 0.1	24	$(C_2H_5)_2CO$ FP	81
***n*-Perfluoropropyl**					
n-C_3F_7/C_2H_5		0.40	87–196	$(n\text{-}C_3F_7)_2CO$ P	82
	(o)	0.021 exp (2.2/RT)	80–256	$n\text{-}C_3F_7COC_2H_5$ P	83
Butyls					
n-C_4H_9/n-C_4H_9		5.	140	$(n\text{-}C_4H_9)_2Hg$ P	84
		0.94 ± 0.05	70–195	$HCOOn\text{-}C_4H_9 + CH_3$	13
		0.95 ± 0.05	75–186	$HCOOn\text{-}C_4H_9 + CH_3$	103
	(p)	$10^{0.6}$ exp (−1.3/RT) 0.95	61–229	$n\text{-}C_4H_9CHO$ P	15
sec-C_4H_9/i-C_3H_7	(r)	0.4	room temp.	$CH_3CH{:}CH_2 + CH_3CH{:}CHCH_3 + H$	107
sec-C_4H_9/sec-C_4H_9	(q)	1.64	25	$CH_3CH_2CH(CH_3)CHO$ P	85
		2.27	100	$(CH_3CH_2CH(CH_3))_2CO$ P	86
		1.5	room temp.	$CH_3CH{:}CHCH_3 + H$	110
		0.95	−103–+25	cis$CH_3CH{:}CHCH_3 + H$	17
		≤ 1.2	107–168	$CH_3CH{:}CH_2 + CH_3$	87
		1.5	24	$CH_3CH_2CH{:}CH_2 + H$	84
		3.5	220	$CH_3CH_2CH{:}CH_2 + H$	84
		0.63 ± 0.08	−78–+25	trans-$CH_3CH{:}CHCH_3 + H$	88
sec-C_4H_9/t-C_4H_9	(r)	0.23	room temp.	$CH_3CH{:}CHCH_3 + (CH_3)_2C{:}CH_2 + H$	107
iso-C_4H_9/iso-C_4H_9		0.42	78–109	$((CH_3)_2CHCH_2)_2CO$ P	86
		0.17 0.17	26–124	$(CH_3)_2CHCH_2CHO$ P	89
t-C_4H_9/C_2H_5	(r)	1.7	room temp.	$CH_2{:}CH_2 + (CH_3)_2C{:}CH_2 + H$	107
		0.31	73–80	$(t\text{-}C_4H_9)_2CO + (C_2H_5)_2CO$ P	62
t-C_4H_9/iso-C_3H_7	(r)	1.2	room temp.	$CH_3CH{:}CH_2 + (CH_3)_2C{:}CH_2 + H$	107
		0.67	72–82	$(t\text{-}C_4H_9)_2CO + (i\text{-}C_3H_7)_2CO$ P	62

Reactants	Notes	*k*dis/*k*comb.	Temperature Range °*C*	Radical Source	Reference
t-C_4H_9/sec-C_4H_9	(r)	2.0	room temp.	$CH_3CH:CHCH_3$ $+(CH_3)_2C:CH_2$ +H	107
t-C_4H_9/t-C_4H_9		4.5	23	$(CH_3)_2C:CH_2$ +H	84
		6.5	300	$(CH_3)_2C:CH_2$ +H	84
		4.59	117–322	$(t\text{-}C_4H_9)_2CO$ P	86
		7.4	20–60	$(t\text{-}C_4H_9O)_2$ P	90
		4.38	27–230	t-C_4H_9CHO P	91
		3.19	50–80	$(t\text{-}C_4H_9)_2CO$ and t-C_4H_9CHO P	62
		2.2 ± 0.3	room temp.	$(CH_3)_2C:CH_2$ +H	107
		3.2			
Monochlorobutyl					
C_4H_8Cl/C_2H_4Cl		0.07	23	$CH_2:CH_2 + COCl_2$ P	68
Pentyls					
n-C_5H_{11}/n-C_5H_{11}		0.2	63	n-$C_5H_{11}COCH_3$ P	22
C_5H_{11}/C_5H_{11}		2.45	25	iso-C_5H_{12} −H	3
		$\geqslant 0.66$	21	n-C_5H_{12} −H	92
cyclo-C_5H_9/cyclo-C_5H_9		0.19	29	cyclo-C_5H_{10} −H	93
		1.0	24	cyclo-C_5H_{10} −H	94
		1.0	26–250	cyclo-C_5H_{10} −H	95
		1.0			
Hexyls					
cyclo-C_6H_{11}/cyclo-C_6H_{11}		0.46	29	cyclo-C_6H_{12} −H	111
cyclo-C_6H_{11}/cyclo-C_6H_{11}	(s)	0.42	29		93
C_6H_{13}/C_6H_{13}		0.97 ± 0.08	25	n-C_6H_{14} −H	4
Amino					
NH_2/NH_2		0.18	no indication	NH_3 F.P.	97
Nitric Oxide					
NO/CH_3O	(t)	0.5	174		96
NO/CH_3CH_2O		0.28	95–135	$(C_2H_5O)_2$ P	96
$NO/(CH_3)_2CHO$	(u)	0.15	26		30
		0.175	79	$(i\text{-}C_3H_7O)_2$ P	30
Iodine atom					
I/C_2H_5		0.33 ± 0.03	28	$(C_2H_5)_2CO + C_2H_5I$ P	98

CHLORINE ATOM TRANSFER

Halogenated Methyl					
CF_2Cl/CF_2Cl		$\leqslant 0.5$	75–119	CF_2ClH −H	99

Disproportionation/Combination Ratios—Continued

Reactants	Notes	*k*dis/*k*comb.	Temperature Range	Radical Source	Reference
			°C		
Halogenated Ethyl					
C_2H_4Cl/C_2H_4Cl		≤ 0.1	26	$C_2H_4+CCl_4$ P	105
	(m)	5.8	23	$C_2H_4+COCl_2$ P	68
$C_2F_2Cl_3/C_2F_2Cl_3$		≤ 0.13	30–70	$CF_2{:}CCl_2+Cl_2$ P	100
C_2H_4Cl/C_4H_8Cl	(n) (v)	0.5	23	$C_2H_4+COCl_2$ P	68
Monochlorobutyl					
C_4H_8Cl/C_2H_4Cl	(n) (w)	4.0	23	$C_2H_4+COCl_2$ P	68

OXYGEN ATOM TRANSFER

Methyl					
CH_3/NO_2		2.0	55–90	$CH_3CHO+NO_2$	101
	(x) (y)	2.4	25	CH_3NO_2 P	102
	(x) (y)	1.8	105	CH_3NO_2 P	102

Notes

(a) Authors consider this value to be too high.

(b) Unpublished work by Thynne.

(c) Author believes the radicals to be vibrationally exited.

(d) *A recalculation of data from Kerr and Trotman-Dickenson,* J. Chem. Soc. 1609 (1960).

(e) Calculated from data of Le Roy and Tickner, J. Chem. Phys. **19**, 1247 (1951).

(f) The temperature dependence gives either *E*dis-*E*comb = − 0.3 kcal/mole or *k*dis/*k*comb = $T^{-0.7}$.

(g) The ethylene formed was more than 90 percent $C_2H_2D_2$.

(h) *Sec*-pentyl is a mixture of the radicals $CH_3CH_2CHCH_2CH_3$ and $CH_3CHCH_2CH_2CH_3$.

(i) *Cyclo*-C_6H_7 is the cyclohexadienyl-1,4 radical.

(j) *Sec*-hexyl is a mixture of the radicals $CH_3CH{-}C_4H_9$ and $C_2H_5CHC_3H_7$.

(k) This value is probably low.

(l) Combination product is $1.4{-}C_4H_8Cl_2$.

(m) Combination product is $1.3{-}C_4H_8Cl_2$.

(n) Combination product is $1.6{-}C_6H_{12}Cl_2$.

(o) Alternatively *k*dis/*k*comb = 0.33 with a large scatter.

(p) Temperature coefficient very doubtful.

(q) In the range 25–243 °C, the results fit the expression *k*dis/*k*comb = 0.715 exp (500/RT).

(r) Very doubtful.

(s) *Cyclo*-C_6H_{11} is the methylcyclopentanyl radical.

(t) Unpublished work by Phillips.

(u) The ratio could be 0.16 within the experimental error of both results.

(v) Products of the disproportionation reaction are C_4H_8 and $1{,}2\text{-}C_2H_4Cl_2$.

(w) Products of the disproportionation reaction are C_2H_4 and $1{,}4\text{-}C_4H_8Cl_2$.

(x) The "disproportionation reaction" is the sum of the rate constants for two reactions viz. (i) $CH_3+NO_2=CH_3ONO$, and (ii) $CH_3+NO_2=CH_3O+NO$.

(y) Combination product is CH_3NO_2.

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Molecule-Molecule Reactions (Hydrogen and Hydrogen Halides)

Reactions	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$H_2 + O_2 = 2OH$		45.0	($k = 84.0$)	485	H_2/O_2 ignition	1
		67.0	14.4	687–807	H_2/O_2 S.T.	2
$H_2 + I_2 = 2HI$	(a)	39.0	14.1	10–235	HI T	3
		41.0	15.09	598–774	H_2/I_2 T	9, 10
			$k = 6.60 \pm 0.09$	394	H_2/I_2 T	11
		41.24 ± 0.25	14.35 ± 0.07	105–360	H_2/I_2 T	12
$D_2 + I_2 = 2DI$	(b) (c)	41.47 ± 0.20	14.14 ± 0.07	360–465	D_2/I_2 T	13
$H_2^p + HI = H_2^\circ + HI$		44 ± 3	13.7	420–480	$H_2/I_2/HI$ T	14
		⩾ 47		420–480	$H_2/I_2/HI$ T	17
$H_2 + NO_2 = NO + H_2O$		18	9.3	384–434	$H_2/O_2/NO_2$ T	15
$HCl + NO_2 = HNO_2 + Cl$		23.4	11.6	100–420	HCl/NO_2 T	23
$HBr + NO_2 = HNO_2 + Br$		13.0	11.0	180–310	HBr/NO_2 T	23
$HBr + C_2F_4 = C_2F_4Br + H$		54.6	16.96	858–1013	$H_2/O_2/C_2F_4Br_2$ S.T.	22
$2HI = H_2 + I_2$	(d) (a)	44.0	13.9	10–235	HI T	3
		49.2	15.56	597–774	HI T	9, 10
		44.20 ± 0.25	13.54 ± 0.07	105–360	H_2/I_2 T	12
$HI + CH_3I = CH_4 + I_2$	(e)	33.4	14.3	270–320	CH_3I/HI T	19
$DI + CH_3I = CH_3D + I_2$			$k = 1.54$	250	$CH_3I/HI/DI$ T	20
$HI + C_2H_5I = C_2H_6 + I_2$	(e)	29.8	13.7	250–300	C_2H_5I/HI T	19
$HI + n\text{-}C_3H_7I = C_3H_8 + I_2$	(e)	19.2	14.1	260–300	$n\text{-}C_3H_7I/HI$ T	19

Ratios of Rate Constants

Reactions	Notes	$E_1 - E_2$	$\log_{10} A_1/A_2$	k_1/k_2	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)			°*C*		
(1) $HBr + CH_2N_2 = CH_3Br + N_2$ (2) $HCl + CH_2N_2 = CH_3Cl + N_2$		−1.5	−0.091		−78–27	$CH_2N_2/HBr/HCl$ T	21
(1) $HI + CH_2N_2 = CH_3I + N_2$ (2) $HBr + CH_2N_2 = CH_3Br + N_2$				4 ± 2	27	$CH_2N_2/HI/HBr$ T	21
(1) $HI + CH_2N_2 = CH_3I + N_2$ (2) $HCl + CH_2N_2 = CH_3Cl + N_2$				50 ± 15	27	$CH_2N_2/HI/HCl$ T	21

Notes

(a) These values summarise a considerable body of early data (references 4 to 8).

(b) For data on the reaction $HD + I_2 = HI + DI$, see reference 16.

(c) For a summary of early data see reference 3.

(d) For data on the reaction $2DI = D_2 + I_2$ see references 13 and 18.

(e) The *A* factor values originally reported (reference 19) are too large by a factor of ten (reference 20).

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Molecule–Molecule Reactions (Hydrocarbons and Hydrocarbon Derivatives)

Reactions	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
Alkanes		*(kcal mole⁻¹)*	*(cm³ mole⁻¹ sec⁻¹)*	°C		
$CH_4 + O_3 =$ products		15.35 13.90	11.21 11.15	35–64 35–64	$CH_4/O_3/O_2$ T CH_4/O_3 T	1 1
$C_2H_6 + C_2H_4 = 2C_2H_5$		68.9	17.6	752–917	$H_2/O_2/C_2H_4$ S.T.	2
Alkenes and aromatics						
$CH_2{:}CHCH{:}CH_2 + C_2N_2 = H_2 +$ 2-cyano pyridine		31.6	12.20	325–450	C_2N_2/C_4H_6 T	3
$CH_2{:}CHCH{:}CH_2 + CF_3CN = H_2 +$ 2-trifluoromethyl pyridine		21.5	9.32	350–520	CF_3CN/C_4H_6 T	4
$CH_2{:}CHCH{:}CH_2 + CF_3CF_2CN = H_2 +$ 2-pentafluoroethyl pyridine		25.0	10.42	340–460	C_2F_5CN/C_4H_6 T	5
$CH_2{:}CHCH{:}CH_2 + CF_3CF_2CF_2CN = H_2 +$ 2-perfluoropropyl pyridine		25.8	10.51	340–460	C_3F_7CN/C_4H_6 T	5
$2C_6H_6 = C_{12}H_{10} + H_2$		40	14.0	900–1210	C_6H_6 T	6
Alkynes						
$2C_2H_2 =$ products	(b)	50.2	16.57	352–472	C_2H_2 T	7
$2C_2H_2 = C_4H_2 + H_2$	(b)	~ 30			C_2H_2 S.T.	8
$2C_2H_2 = C_4H_2 + H_2$	(b)	36.4 ± 3	12.89	1127–2227	C_2H_2 S.T.	9
$2C_2H_2 = C_2H_2^* + C_2H_2$	(b)	50	14.04	1227–2227	C_2H_2 S.T.	10
$2C_2H_2 = C_4H_3 + H$	(b) (a)	38.8 ± 7.5 41.6 ± 0.6	13.47 ± 0.78 13.77 ± 0.11	1630–1922 347–2177	C_2H_2 S.T.	11 11
Hydrocarbon derivatives						
$CH_3CHO + O_2 = HO_2 + CH_3CO$		29 ± 2		320–380	CH_3CHO/O_2 T	12
$CH_3I + I^*{-}I = CH_3I^* + I_2$	(c)	9.0	6.40	60–140	CH_3I/I_2 T	13
$CH_3OCH_3 + NO = HNO + CH_2OCH_3$		43.4	14.0	500–600	CH_3OCH_3/NO T	14

Notes

(a) Critical review of literature data.

(b) These values are included in the review estimate (a), the products of the reaction being considered to be $C_4H_3 + H$.

(c) These values may be low because of complicating heterogeneous reactions.

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Nitrogen Dioxide (Molecule–Molecule Reactions)

Reactions	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°*C*		
$NO_2 + H_2 = NO + H_2O$		18.	9.3	384–434	$H_2/O_2/NO_2$ T	19
$NO_2 + HCHO = HNO_2 + HCO$		15.1	10.1	118–160	$HCHO/NO_2$ T	20
$NO_2 + CHOCHO = HNO_2 + COCHO$		19.8	11.9	160–210	$CHOCHO/NO_2$ T	21
$NO_2 + CH_3CHO = HNO_2 + CH_3CO$		16.0	12.9	118–143	CH_3CHO/NO_2 T	22
$NO_2 + NH_3 = HNO_2 + NH_2$		27.5	12.7	327–527	NH_3/NO_2 T	1
$NO_2 + HCl = HNO_2 + Cl$		23.4	11.6	100–420	HCl/NO_2 T	2
$NO_2 + HBr = HNO_2 + Br$		13.0	11.0	180–310	HBr/NO_2 T	2
$NO_2 + F_2 = NO_2F + F$		10.5	12.2	28–70	NO_2/F_2 T	7
$NO_2 + F_2O = NO_2F + FO$		14.48	11.11	60–80	F_2O/NO_2 T	18
$NO_2 + Cl_2O = NO_2Cl + OCl$		11.6	10.64	20–60	NO_2/Cl_2O T	3
$NO_2 + ClO_2 = NO_3 + OCl$		11.5	10.68			3
$NO_2 + NOCl = NO + NO_2Cl$		10.0	10.28	−20–+8	$NOCl/ClO_2$ T	4
$NO_2 + CO = CO_2 + NO$		31.6	13.08	267–454	CO/NO_2 T	5
		27.8	11.68	225–290	CO/NO_2 T	6
$NO_2 + O_3 = NO_3 + O_2$		7.0	12.77	13–29	O_3/NO_2 T	8
			$k = 1.96 \times 10^7$	room temp.	O_3/NO_2 T	9
$2NO_2 = NO + NO_3$			$k = 2.6 \times 10^4$	434	NO_2 T	10
		23.90 ± 0.60	11.89 ± 0.25	200–430	NO_2 T	11
	(a)	23.				12
$2NO_2 = 2NO + O_2$	(b)	27.10	12.69	320–380	NO_2 T	13, 11
		26.90	12.60	357–747	NO_2 T	14, 11
		26.90 ± 0.10	12.60 ± 0.04	200–550	NO_2 T	11, 10
$2NO_2$ = products	(c)	25.6	11.8	319–383		15
	(c)	25.0 ± 5.0	13.40	1127–2027	NO_2 S.T.	16
	(c)	25.7	12.95	1227–1827	NO_2 S.T.	17

Notes

(a) Estimated from the reverse reaction.

(b) These values were recalculated from the original data (reference 11).

(c) These values represent the sums of the contributions from $2NO_2 = 2NO + O_2$ and $2NO_2 = NO + NO_3$.

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Molecule–Molecule Reactions (Inorganic Molecules)

Reactions	Notes	E	$\log_{10} A$	Temperature range	Radical source	Reference
		($kcal\ mole^{-1}$)	($cm^3\ mole^{-1}\ sec^{-1}$)	°C		
$F_2+CO=FCO+F$		13.5 ± 1.2	11.67	15–45	$F_2/CO/O_2$ T	1, 2
$F_2+ClO_2=FClO_2+F$		8.5 ± 0.4	10.6	−46–−26	F_2/ClO_2 T	3
		8.0 ± 0.5	10.11	−46–−26	F_2/ClO_2 T	4
$Cl_2+O_3=ClO+ClO_2$		26.0 ± 1		35–60	Cl_2/O_3 T	5
$2ClCN=Cl_2+C_2N_2$		60.	13.	1727–2527	ClCN S.T.	6
$2NOCl=Cl_2+2NO$		23.4	12.5	150–250		7
		23.6 ± 0.7	12.7 ± 0.3	150–411	NOCl T	8
$2NOI=I_2+2NO$		$k\leqslant4\times10^{10}$		60	NO/I_2 F.P.	15
$2O_3=3O_2$		18.8	12.65	70–100	O_3 T	9
$CO+O_2=CO_2+O$		51.0 ± 7.0	12.54 ± 0.22	2127–2727	CO/O_2 S.T.	10
$CO+B_2H_6=BH_3+BH_3CO$	(a)	17.65	11.32	0–60		11
$BF_3+BCl_3=BF_2Cl+BFCl_2$		$k\approx5\times10^{3}$		23	BF_3/BCl_3 T	12
$PH_3+B_2H_6=PH_3BH_3(g)+BH_3$		11.4	9.5	−24–0	PH_3/B_2H_6 T	14, 13, 11

Notes

(a) Critical review of literature data.

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Termolecular Reactions

Reactions	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{6} *mole*$^{-2}$ *sec*$^{-1}$)	°*C*		
$2NO + O_2 = 2NO_2$	(a)	$k = (7.45 \pm 0.22) \times 10^9$		25	NO/O_2 T	1
		$k = 6.0 \times 10^9$		25	NO/O_2 T	2
		$k = 7.10 \times 10^9$		25	NO/O_2 T	3
$2NO + Cl_2 = 2NOCl$	(b)	4.2	10.4			8, 9
		6.0	11.4	100–250	NO/Cl_2 T	10
$2NO + Br_2 = 2NOBr$		1.6	10.6	−8–15	NO/Br_2 T	11, 8
$2NO + H_2 = \text{products}$	(c)	47	18.7	700–825	NO/H_2 T	12, 8
$NO + NO_2 + O_2 = NO_2 + NO_3$		$k = 6.58 \times 10^7$		25	$NOCl/NO_2/O_2$ T	13
	(d)	$k = 3.0 \times 10^7$				15
		−0.96	7.32	200–430	NO_2 T	14
$2NO_2 + O_2 = 2NO_3$	(e)	25	($k = 7 \times 10^{-12}$)	27		15
$H + O_2 + H_2 = H_2O + OH$		$k = 2 \times 10^{11}$		830–1630	H_2/O_2 S.T.	16
$CF_3NO + 2NO = CF_3 + N_2 + NO_3$		$k = 5.6 \times 10^5$		24	CF_3I/NO P	17
$CH_3NO + 2NO = CH_3 + N_2 + NO_3$	(f)	−1.8	6.41	25–70	CH_3I/NO P	18
$C_2H_5NO + 2NO = C_2H_5 + N_2 + NO_3$	(f)	−2.9	6.28	25–70	C_2H_5I/NO P	18
$CH_3CH_2CH_2NO + 2NO = CH_3CH_2CH_2 + N_2 + NO_3$	(f)	−7	3.7	25–45	C_3H_7I/NO P	18
$(CH_3)_2CHNO + 2NO = (CH_3)_2CH + N_2 + NO_3$	(f)	−4	5.3	25–45	$(CH_3)_2CHI/NO$ P	18
$(CH_3)_3CNO + 2NO = (CH_3)_3C + N_2 + NO_3$	(f)	−7.5		25–70	$(CH_3)_3CI/NO$ P	18

Notes

(a) Further data on this reaction can be found in references 4 to 7.

(b) Critical survey of literature data. The Arrhenius plot is curved, and the values given are valid only at low temperatures.

(c) It is unlikely that the nitric oxide-hydrogen reaction is a simple termolecular process.

(d) Temperature independent. Estimated from the reverse reaction.

(e) Estimated from the reverse reaction.

(f) These values are for an overall reaction which could be $RNO + NO \rightleftharpoons R(NO)_2$; $R(NO)_2 + NO = R + N_2 + NO_3$.

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Inversion (Group Transfer) Reactions

Reactions	Notes	E	$\log_{10}A$	Temperature range	Radical source	Reference
		(*kcal mole*$^{-1}$)	(*cm*^{3} *mole*$^{-1}$ *sec*$^{-1}$)	°C		
$^{14}CH_3 + CH_3COCH_3 = {}^{14}CH_3COCH_3 + CH_3$	(a)	$k = 5.2 \times 10^6$		350	CH_3COCH_3 P	1
$CH_3 + CF_3COCF_3 = CH_3COCF_3 + CF_3$		5.7 ± 1.5	9.3	163–245	$CH_3N_2CH_3$ P and T	2
		6.2 ± 1.0	11.4	85–210	CF_3COCF_3 P	3
		7.0 ± 1.0	11.7	48–240	CH_3COCH_3/CF_3COCF_3 P	4
$CH_3 + C_2F_5COC_2F_5 = CH_3COC_2F_5 + C_2F_5$		7 ± 1		184–240	$(C_2F_5)_2CO$ P	5
$CD_3 + CH_3HgCH_3 = CD_3HgCH_3 + CH_3$		$k = 8.9 \times 10^5$		180	CD_3COCD_3 P	6, 7
$CH_3 + CD_3SH = CH_3SH + CD_3$		7.6	10.73	130–200	CH_3COCH_3 P	8
$CH_3 + CF_3COCH_3 = C_2H_6 + CF_3CO$		14.		150–350	CF_3COCH_3 P	9
$CH_3 + CH_3COCOCH_3 = CH_3COCH_3 + CH_3CO$		5.6	10.7	100–200	$CH_3COCOCH_3$ P	10
		6.6		100–200	$CH_3COCOCH_3$ P	11
$CH_3 + CH_3CH{:}CHCHO = CH_3CH{:}CHCH_3 + CHO$		7.45 ± 1.30	11.8 ± 0.4	120–250	CH_3COCH_3 P	12
$CH_3 + CH_3HgCH_3 = C_2H_6 + (Hg + CH_3)$		1.0	7	175–220	$(CH_3)_2Hg$ P	13, 14
$C_6H_5 + C_6H_5COCH_3 = C_6H_5C_6H_5 + CH_3CO$	(b)	6.2	9.6	277–407	$C_6H_5COCH_3$ P	15
$CF_3CH_2O^{15}NO + {}^{14}NO = CF_3CH_2O^{14}NO + {}^{15}NO$		23.7 ± 0.5	12.78	130–150	$CF_3CH_2O^{15}NO/{}^{14}NO$ T	16
$CH_3CH_2O^{15}NO + {}^{14}NO = CH_3CH_2O^{14}NO + {}^{15}NO$		$21.4 \pm + 0.5$	11.48	130–150	$CH_3CH_2O^{15}NO/{}^{14}NO$ T	16
$BH_3 + B_2D_6 = BH_3BD_3 + BD_3$		6.0	14.2	24–44	B_2H_6/B_2D_6 T	17, 14, 21, 22
		7.8	13.45			18
$BH_3 + BH_3CO = B_2H_6 + CO$		7.0	11.4	0–30	BH_3CO T	19, 17, 22
$PH_3 + B_2H_6 = BH_3PH_3 + BH_3$		11.4 ± 2	9.5	−24–0		20, 22

Notes

(a) Assuming $k=10^{11.6}$ exp $(-9800/RT)$ for the reaction $CH_3+CH_3COCH_3=CH_4+CH_2COCH_3$.

(b) C_6H_5 refers to the phenyl radical.

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