A Critical Review of H-Atom Transfer in the Liquid Phase: Chlorine Atom, Alkyl, Trichloromethyl, Alkoxy, and Alkylperoxy Radicals

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This review covers hydrogen-atom transfer from carbon-hydrogen bonds in organic compounds to chlorine atom, methyl, ethyl, trichloromethyl, t-butoxy and alkylperoxy radicals in the liquid phase. Rate constant data are presented in 38 tables. Literature is covered through most of 1972. The review is divided into six sections; an introduction plus five sections each dealing with specific radicals. Hydrogen-atom transfer to chlorine atom are presented as relative rate constants. For hydrogen-atom transfer to methyl, ethyl, trichloromethyl, and t-butoxy radicals, both relative and absolute rate constants are tabulated. For alkylperoxy radicals only absolute rate constants are listed. Each absolute rate constant has a tabulated set of rate parameters where A has been assigned and E derived from the Arrhenius equation.

Key words: Chlorine atom reactions; hydrogen transfer reactions; liquid phase; organic molecules; organic radical reactions; rate constants; reference data.

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1. Introduction

The objective of this review is to collect the best available rate constants for hydrogen-atom transfer from carbon-hydrogen bonds in organic compounds to chlorine atoms, small alkyl radicals, trichloromethyl, alkoxy, and alkylperoxy radicals in the liquid phase. We also evaluate the limits of uncertainty and assign or calculate Arrhenius A-factors and activation energies (activation parameters) for all absolute rate constants and selected relative rate constants. Excluded from this review are H-atom transfer from carbon to carbon during polymerization (chain transfer) and from elements other than carbon.

1.1. Background

Ever since the early 1930s when chemists first recognized the important role of free radicals in many chemical processes, much effort has gone into measurements of rates of the elementary steps involving atomic and molecular radicals. The objective has been to develop generalizations concerning structure and reactivity that would be useful in prediction as well as in understanding. Only in the last few years, however, has this goal been even partly realized owing to the experimental difficulties and the complexities of the problem.

One of the most important classes of free radical reactions is hydrogen atom transfer, usually from carbon to another radical center as represented by the reaction

$$X\cdot + H\text{—}\overset{|}{\underset{|}{C}}\rightarrow XH + \cdot\overset{|}{\underset{|}{C}}\text{—},$$

where X might be carbon, oxygen, nitrogen, sulfur, or halogen. Although these reactions represent a significant proportion of free radical chemistry and are the subject of hundreds of papers, surprisingly few sources of reliable kinetic parameters (entropies and enthalpies of activation) are available either on a relative or an absolute basis for these reactions. For gas phase systems, the recent reviews by Trotman-Dickenson and Milne [1] [1] and the selected series of critical reviews by the group at the University of Leeds [2] are among the best sources available. For liquid phase systems, there is nothing comparable, although Howard's [3] more circumscribed review of $RO_2\cdot$ and $RO\cdot$ radicals is among the most extensive and reliable for any class of radical reactions, and Denisov's grand compilation [4] is unrivaled for completeness.

One of the important unsolved problems of radical chemistry is the quantitative effect of phase on the absolute rate of a reaction. Thus, while reliable absolute rate constants are now available for reactions of halogen atoms and alkyl radicals in the gas phase, almost none are available for these radicals in the liquid phase. The converse is found for reactions of alkylperoxy radicals, where many reliable values are available for the liquid phase but almost none have been measured in the gas phase. For lack of a reliable basis for converting absolute rate data from gas to liquid phase, most of the published data for chlorine atom and alkyl radicals must remain on a relative basis.

[1] Figures in brackets indicate the literature references, which are listed at the end of each section.

1.2. General Kinetic Treatments

A general radical chain sequence for H-atom transfer involves simultaneous initiation, propagation, chain transfer, and termination reactions. For example, the halogenation of substrate RH by the halogen X_2, may be expressed by the following reactions

$$\text{Initiation} \qquad X_2 \xrightarrow{k_i} 2X\cdot \tag{1}$$

$$\text{Propagation} \qquad X\cdot + RH \xrightarrow{k_a} XH + R\cdot \tag{2}$$

$$\text{Transfer} \qquad R\cdot + X_2 \xrightarrow{k_b} RX + X\cdot \tag{3}$$

$$\text{Termination} \qquad 2X\cdot \xrightarrow{k_{t1}} \tag{4}$$

$$X\cdot + R\cdot \xrightarrow{k_{t2}} \text{Termination Products} \tag{5}$$

$$2R\cdot \xrightarrow{k_{t3}} \tag{6}$$

For the case where the chain length is long, i.e., rates of reactions (2) and (3) are much greater than the sum of rates for the termination reactions, the general equation governing this set of reactions is conveniently solved in the form [5]

$$[RH]^2 R_i/R_{RH}^2 = \frac{2k_{t1}}{k_a^2} + \frac{2k_{t2}}{k_a k_b}\left(\frac{[RH]}{[X_2]}\right) + \frac{2k_{t3}}{k_b^2}\left(\frac{[RH]}{[X_2]}\right)^2, \tag{7}$$

where brackets represent concentrations of X_2 and RH and $R_i = k_i[X_2]$ and $R_{RH} = -d[RH]/dt$.

For special cases where rates of reactions (5) and (6) are small relative to (4), $[R\cdot] \sim 0$, eq (7) simplifies to a more familiar form commonly applied to oxidation and polymerization chain reactions

$$R_{RH} = \left(\frac{R_i}{2k_{t_1}}\right)^{1/2} k_a[RH]. \tag{8}$$

Both equations may be used to evaluate $k_a/(2k_{t1})^{1/2}$ if values for R_i and R_{RH} are known or can be measured. Absolute values of k_t^1 can be evaluated directly from the steady-state radical concentration or indirectly by one of the non-steady state techniques. Absolute values can then be assigned to k_a (hereafter referred to as simply k). As yet there have been no direct measurements of rate constants for abstraction of a H-atom from carbon.

Equation (7) has been used to evaluate k for t-BuO· radical generated from t-BuOCl [5] and could be applied to halogenations as well; eq (8) is used extensively in kinetics analyses of autoxidation reactions [6]. But many other radical abstractions result in systems too complex to be amenable to this kind of kinetic analysis or the kinetic chain lengths are too short for eqs (7) or (8) to be applicable. In such cases rates of formation for only certain propagation and termination products will provide values for $k/k_t^{1/2}$ without additional knowledge of the other products. From reactions (2) and (4), where their rates are known from product analyses,

$$R_2/R_4^{1/2} = k[RH]/k_t^{1/2}. \tag{9}$$

Equation (9) could be used to evaluate k for some alkyl radicals since k_t has been recently reported for combination of some radicals in solution [7].

The user will find that more than half the entries in this review are for relative rate constants, often compared with a common standard, but without any reliable means of converting the relative values to absolute values. For chlorine atom abstractions, where absolute rate constants are known for gas phase but not for liquid phase systems, we have not used gas phase data as a basis for deriving liquid phase absolute rate constants because there appears to be no sound basis for such interconversion at this time. Inspection of the tables on chlorine atom abstraction shows that only a few absolute values for abstraction are needed to put all relative values on an absolute basis. The situation is similar for the methyl and ethyl radicals except there is a limited amount of data where eq (9) can be used. From the information that is available we have evaluated k for a number of reactions in different solvents but with some uncertainty.

1.3. Activation Parameters

Throughout this review we have attempted to include measured values for Arrhenius A-factors and activation energies, E, as defined by the Arrhenius equation

$$\log k = \log A - (E/2.3RT)$$
$$(R = 8.314\ \text{J}\cdot\text{mol}^{-1}\cdot K^{-1} = 1.986\ \text{cal}\cdot\text{mol}^{-1}\cdot K^{-1})$$

In only a few cases, however, are such values reported explicitly; for chlorine atom reactions, most temperature dependent data are not accurate enough to use in calculating relative values of A and E. However, several sets of parameters were calculated for reactions of chlorine atoms in noncomplexing solvents.

For most radical reactions, however, reliable data are available at only one temperature. Therefore, we have assigned values of log A based on the probable change in entropy of a reactant going to the transition state for H-atom transfer to a radical species. Detailed treatments of bimolecular atom-transfer processes by Benson [8] and Golden [9] suggest that for H-atom transfers involving polyatomic radicals, log $(A/M^{-1}s^{-1})$[2] should be no lower than 8 to 9 for alkanes and no lower than 7 to 8 for open-chain allylic or benzylic systems where greater stiffening in the transition state for these latter reactants will increase $\Delta S^{\pm}$ and lower log A by about one

[2] Throughout this paper the units symbol M is equal to mol · dm^{-3}.

log unit [8 and 9]. There is good experimental evidence that log $(A/M^{-1}s^{-1}) \geq 9$ for sec-H-atom transfer from alkanes to $RO_2 \cdot$ radicals [10]. These H-atom transition states should have the largest degree of bond breaking of any of the common H-atom transfers owing to the high activation energies (> 10 kJ/mol). Accordingly we would expect the largest effects of resonance on $\Delta S^{\pm}$ to be found here, and we have assigned values of log A for all H-atom transfers as shown in table 1.1 with an additional refinement (perhaps unjustified) that values of log A for secondary (sec) and tertiary (tert) H-atom transfers are larger by 0.2 and 0.4, respectively, than for primary (prim) H-atom transfers. Several kinds of H-atom transfers exhibit this structural effect in gas phase reactions [11], and some support for these differences also comes from reactions of methyl radical in the liquid phase [12].

TABLE 1.1. Assigned value of log A for H-atom transfer to polyatomic radicals

Reactant	log $(A/M^{-1}s^{-1}) \pm 0.5$ [b]
Alkyl pri	9.0
sec	9.2
tert	9.4
Allyl pri	8.0
sec	8.2
tert	8.4
Benzyl pri	8.0
sec	8.2
tert	8.4
Cycloalkyl sec	9.2
tert	9.4
Cycloallyl sec	8.7
tert	8.9
Cyclobenzyl sec	8.7
tert	8.9
Heterosubstituted [a]	8.7

[a] Includes ethers, alcohols, sulfur analogs, amines, and aldehydes. Where reliable experimental evidence indicates that some other value of log A is applicable, we have also listed the experimental value (by way of recognizing that kinetics is as much an art as a science). However, in no case do the estimated and experimental values differ by more than one log unit and larger differences, which are often reported, should be viewed with considerable skepticism.

[b] M = mol · dm^{-3}.

Intermediate values of log A were assigned to reactions involving cyclic allyl and benzyl systems and to heteroatom substituted systems on two bases: For cyclic systems, changes in $\Delta S^{\pm}$ should be smaller than for open chain systems since resonance stabilization cannot additionally stiffen these structures very much. In heteroatom systems where resonance effects involving p-electrons appear to be small as indicated by only small changes in CH bond strengths on substituting oxygen or nitrogen for carbon [13], we have increased log A to 8.7 to reflect a lessened degree of resonance interaction but have neglected differences between pri, sec, and tert CH bonds. We believe this procedure, with a probable error of ± 0.5 log unit, is at least as reliable as most rate measurements over limited temperature spans and for some radical systems, such as alkylperoxy or alkoxy, the most reliable method of obtaining rate parameters. The values of log A for the relative reactivities (k) for the chlorine atom reaction have been assigned as the difference in the expected value of log A from the individual values of log A in table 1.1. However the actual value of log A for the chlorine atom will be at least a log unit of 1 larger because of a smaller change in $\Delta S^{\pm}$ associated with these reactions.

From the experimental value of either the absolute or relative k and the assigned value of log A we have calculated E with the precision needed to recalculate the original value of k.

1.4. Error Analysis

Because many different kinds of experimental procedures are used to measure radical abstraction processes, no one error analysis procedure is applicable to all sets of data. Relative reactivity data reported for chlorine atom abstraction appear to be of high precision, often with less than 2 percent standard deviation (see section 2). But absolute values for k for abstraction by t-BuO · radical are probably not accurate to better than a factor of three owing to the uncertainties in the kinetics of t-BuOCl chlorinations [5]. Other rate constants have precision and accuracies that lie between these extremes, but it is unlikely that any absolute value of k can be considered reliable within a factor of two. Some sets of experimental data are reported with error limits that involve a judgmental factor in selection of data. These error limits may be considered as equal to twice standard deviation.

Most experimental measurements of E are made over temperature spans of 40–80 K and usually around 298 K. Benson's "rule" [14] indicates that with a random error of 20 percent in k (relative) E may be determined with an accuracy of about 30 percent; however, with a random error of 100 percent in k (absolute), E is only accurate to 1100 percent or a factor of 10! This latter value is discouraging if one hopes to measure accurate values for E from temperature dependence of k (absolute). It is mainly for this reason that we have preferred to rely predominantly on assigned values of A and calculated E (absolute).

We estimate that assigned values of log A are accurate to ± 0.5 log units or a factor of 3 in A. Combined with a random error of ± 100 percent in k (absolute), the error in E (absolute) is 4.6 KJ/mol (1.1 kcal/mol) if k is evaluated at 298 K. The interdependence of A and E is such that, at the temperature used to calculate E, the errors cancel and we have calculated E from k and A with enough precision to enable the user to recalculate the original value of k. Compensation of errors is increasingly poor as the temperature departs from the point of evaluation. In most cases, if k is calculated at temperatures within 100 degrees of the temperature where

E was evaluated, the uncertainty in $\log A$ (± 0.5) results in less than a factor of 2 in the uncertainty in k.

1.5. Literature Sources

A thorough search of *Chemical Abstracts* was made through 1972 under the major subject headings for specific radicals. A few data on trichloromethyl radical are current through May 1973. The review on oxy radicals by Howard [3] is the major source of data for H-atom transfer by those radicals. Both of these sources were supplemented by a search of the holdings of the Chemical Kinetics Information Center at the National Bureau of Standards by Francis Westley. Supplemental data for chlorine atom were obtained from a review by Poutsma [15].

1.6. Format

The review is divided into five data sections plus the introduction. To assist the user, references are renumbered in each section and listed in the back of each section. Although every effort has been made to use a consistent format throughout, some differences among tables are unavoidable owing to differences in the kinds and reliability of data available for various radicals.

In the tables, compounds are generally grouped by type, such as alkane, substituted alkanes, cycloalkane, aralkanes, and miscellaneous compounds. In each grouping, compounds are listed in order of increasing complexity generally according to IUPAC nomenclature.

In those cases where relative rate constants are reported, the reference compound and position are indicated in the Standard column. If reactivity is relative to a second position in the same molecule, only the position is indicated in the column. In table 2.1 all reactivity data are relative to one standard indicated in the heading, and therefore we have deleted the Standard column.

Rate constants k are expressed in $M^{-1}s^{-1}$ (see footnote 2). For those cases where rate constants are expressed relative to a second reaction ($k=k_s$) with the same order in free radical (k/k_s), the values are dimensionless. Very large and very small values of k are listed as partial exponents. Thus a column heading 10^3k requires that every listing in that column be multiplied by 10^{-3} to retrieve k. Every effort was made to list k and (k/k_s) on a *per CH basis*. The values of log A, log (A/A_s), E, and $E-E_s$ are Arrhenius constants that best fit the kinetic data according to the Arrhenius equations

$$\log k = \log A - E/2.303RT$$

or

$$\log (k/k_s) = \log (A/A_s) - (E-E_s)/2.303RT.$$

The units of A are the same as for k, the units for A/A_s are dimensionless; the units for E or $E-E_s$ are in SI units of kilojoules per mole (kJ/mol) with the more common value of kilocalories per mole (kcal/mol) in parentheses. To minimize confusion we use only kcal/mol in the text. In those few cases where temperature dependent data are available and reliable, values of log A and E are calculated from the best fit of the data to the Arrhenius equation (log k versus $1/T$). In most cases however, log A is assigned (see table 1.1) and E is calculated for absolute values of k but not for relative values of (k/k_s).

We have, as a general rule, not repeatedly listed standard, solvent, temperature, or reference when the same listing applies to several entries in sequence.

1.7. Unsolved Problems in H-Atom Transfer

Little effort has been made to determine absolute rate constants for H-atom transfer reactions by small free radicals in the liquid phase except in the case of peroxy radicals. Until recently this lack of information was due partly to the unavailability of suitable techniques and the difficulty of performing such measurements. In addition liquid phase radical chemistry was more the province of organic chemists whose orientation is toward the products of reaction and the relation of products to substrate structure. Thus relative reactivity was adequate to answer many questions especially when confronted with the difficulties of obtaining absolute rate constants.

At this time knowledge of absolute rate constants is becoming more important, particularly in evaluating critical steps in chemical processes and in actually modeling such processes to maximize efficiency. However, as seen in this review, such information is limited. Thus, while this review attempts to show what information is available, equally important it also shows what is not available.

Perhaps the most glaring deficiency is the absence of any absolute rate data for H-atom transfers to chlorine atom. The information on relative reactivity seems to suggest that rate constants in solution are slower than in the gas phase, but no one has pursued this question in sufficient detail to overcome the experimental difficulties.

The information we have on the methyl radical is preliminary; however, these data appear to be fairly consistent with the gas phase data considering the experimental uncertainties. Techniques are readily available to put the absolute rate data on more certain bases and should be done. Some additional information on the other alkyl radicals is also justifiable.

The various sources of data on the liquid phase reactions of the trichloromethyl radical show reasonable agreement. The most interesting problem in this case is why rate constants for gas and liquid phase reactions differ.

The absolute rate data for alkoxy radicals is limited largely to the t-butoxy radical and that relies on two measurements of the combination of two t-butoxy radicals, which agree only within a power of 10. Thus while the data could be improved, we probably know these rate constants within a factor of 3.

More information is available on the absolute rate con-

stants of peroxy radical reactions in solution than on any other small radical. While greater precision would be desirable, it is not likely that the data can be significantly improved until new techniques are developed.

While the absolute rate data for H-atom transfers by various free radicals in the liquid phase are in various degrees of development, at least two questions common to all radical abstraction reaction are important. First with the present data we can generally estimate the Arrhenius A values with greater accuracy than they can be determined experimentally. In general data have not been obtained over a sufficient temperature range to give the desired precision in A. Thus more attention should be given to improving precision and to increasing the temperature range of the measurements so that experimental A values can be made more reliable.

The second and the most interesting problem deals with the effect of phase change on the rate constant. While for example Russell [16], and others later, showed that aromatic solvents can have profound effects on the relative reactivity toward the chlorine atom, we cannot tell how much effect these solvents have on the rate constants compared with absence of solvent or what effect so called "non-complexing" solvents have relative to absence of solvent, if any. This question has been considered by Mayo [17], who discussed mainly the differences between phases, such as concentration differences, and the effects of free volume, cages, and third-body interactions. However, the need still exists to quantify the differences on individual steps by measuring their rate constants in both phases under parallel conditions.

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2. Reactions of Chlorine Atoms

While there has been considerable interest in the reactions of chlorine atoms with organic compounds, there has been no direct measurement of any absolute rate constants for reactions of chlorine atoms with substrates in solution. Kinetic studies that in principle could give rate constants have led to results that suggest that the reactions are inhibited by trace impurities [1 and 2]. The expected chain lengths of liquid phase reactions, based on gas phase data, are expected to be in the range of 10^6 to 10^{10}. Thus the reactions should be sensitive to small amounts of inhibitors such as oxygen, phenols, and amines.

Because of the limitations in obtaining absolute rate constant data (section 1), most effort has been made to measure the relative reactivity of different compounds and of different positions within a single molecule toward chlorine atoms. This type of information is relatively easy to obtain without any significant interference from the problem mentioned above, and it does indicate the effects of substrate structure on reactivity. However, it is of no value for estimating the absoulte rate constants or for predicting how abstraction of hydrogen would compete with termination reactions.

2.1. Determination of Relative Reactivities

For two competing reactions of a chlorine atom

$$\mathrm{Cl}\cdot + \mathrm{R_1H} \xrightarrow{k_1} \mathrm{HCl} + \mathrm{R_1}\cdot$$

$$\mathrm{Cl}\cdot + \mathrm{R_2H} \xrightarrow{k_2} \mathrm{HCl} + \mathrm{R_2}\cdot$$

the expression for the relative disappearance of the two hydrocarbons on a molecular basis is

$$d[\mathrm{R_1H}]/d[\mathrm{R_2H}] = (k_1/k_2)\ [\mathrm{R_1H}]/[\mathrm{R_2H}].$$

Separation of the variables and integration gives

$$k_1/k_2 = \{\log[\mathrm{R_2H}]_0/[\mathrm{R_2H}]\}/\{\log\ [\mathrm{R_1H}]_0/[\mathrm{R_1H}]\}.$$

An approximate, but somewhat simpler, expression often used is

$$k_1/k_2 = \frac{\Delta[R_1H]}{\Delta[R_2H]} \times \frac{[R_2H]_{av}}{[R_1H]_{av}} = \frac{[R_1Cl]}{[R_2Cl]} \times \frac{[R_2H]_{av}}{[R_1H]_{av}}.$$

This simpler expression generally gives satisfactory results up to about 20% conversion, above which the error increases rapidly with conversion unless both reactants have nearly the same reactivity.

The relative reactivity on the molecular basis is related to the reactivity on a per active hydrogen by the relationship

$$(k_1/k_2)_{\text{molecular}} = (n_1/n_2)\ (k_1/k_2)_{\text{hydrogen}},$$

where n_1 and n_2 are the number of reactive hydrogens *in reactants* R_1H and R_2H, respectively. In all cases reactivities are reported here on the per active hydrogen basis.

Thus the general technique for evaluating k_1/k_2 involves measuring the formation of the products at low conversions or the decrease of reactants at higher conversion. When the products are used to estimate the relative reactivity of the initial reactants, the reactivity of the products become important. If the initial product of one of the components has the same reactivity as the initial component, at 5 percent conversion the initial product would react 0.052 as fast as it is formed; at 10 percent conversion it would react 0.111 as fast. Since in most cases the monochlorinated materials are less reactive than the original material, further chlorination of the initially formed products is of little importance below 10 percent conversion.

When the change of reactants is being followed, secondary reaction of the products is not generally a problem, and high conversions are necessary to obtain satisfactory accuracy in the relative reactivity ratio. Generally 50 percent conversion of both reactants is necessary to reduce the uncertainties in k_1/k_2 to below 10 percent.

The above error analysis is based on optimum analytical conditions. In fact serious nonrandom errors can be introduced in determining the chloride products or the disappearance of reactants. The standard procedure generally has been to use gas chromatography (gc). However, under the conditions necessary for gc analysis (higher temperatures and potential catalytic surfaces), complications can result from the ease with which most organic chlorides can eliminate hydrogen chloride. While an analysis may give reproducible results, there may be systematic errors. Undoubtedly many research groups have made efforts to eliminate complications during the gc analysis, but it is unfortunate that they have not generally made note of this in their publications.

An alternative method of analysis for cases where one of the products is highly reactive and would dehydrohalogenate easily during a gc analysis is to determine one or both chlorides by selective hydrolysis. Because of the larger uncertainties associated with this approach, this method should be used only when gc methods are inadequate.

2.2. Solvent Effects

Unlike most other atomic or molecular radicals, the relative reactivity and undoubtedly the absolute rate constants of the chlorine atom are very sensitive to the composition of the solvent [3]. The selectivity increases in the presence of a solvent or substrate that can complex with the electron-deficient chlorine atom. This selectivity effect is a function of concentration of the complexing solvent or substrate as well as the strength of the complex. Aromatic compounds and CS_2 complex strongly with chlorine atoms with the result that relative reactivities measured in these solvents are difficult to interpret in terms of relative rate parameters. Therefore although values for log (A/A_s) and $-(E-E_s)$ could be readily assigned and calculated at each complexing solvent concentration, we have not done so. Rate parameters for chlorine atom reactions in noncomplexing solvents have been calculated and appear in table 2.1 (see next section).

2.3. Relative and Absolute Rate Parameters

In the analysis of data obtained in noncomplexing solvents, such as alkanes, carbon tetrachloride, and nitrobenzene, the assumption is made that the statistically corrected values of A for the reaction of chlorine atom are different for each type of carbon-hydrogen bond (primary, secondary, and tertiary). This assumption draws support from gas phase data where for several radicals the values of A for tertiary, secondary, and primary differ by factors of 2 to 4 [4]. Figure 1 is a plot of liquid-phase data where secondary and tertiary C–H bonds are compared directly with the primary C–H bonds in the same molecule. These data indicate that A_{sec}/A_{pri} ratios are greater than unity but not more than 2. Since we feel the variation could easily be the result of experimental uncertainties, in our analysis we have used

$$\log A_{tert}/A_{pri} = \log A_{sec}/A_{pri} = 0.15.$$

Using these values of A_{tert}/A_{pri} and A_{sec}/A_{pri} one may calculate $E_{tert} - E_{pri}$ and $E_{sec} - E_{pri}$ for various reactions from data at one temperature. In table 2.1 the differences in E have been determined in this way. Since ratios of log A have an uncertainity of ± 0.15, a general uncertainty is introduced into ΔE of about ± 0.2 kcal/mol. However, because of the interdependence of errors in A and E, the errors completely compensate at the temperature where they were evaluated. The compensation is poorer the farther the temperature is from the point of evaluation. Thus at 50 K from the evaluation temperature the uncertainty is generally ± 30 percent in a calculated value of a relative reactivity.

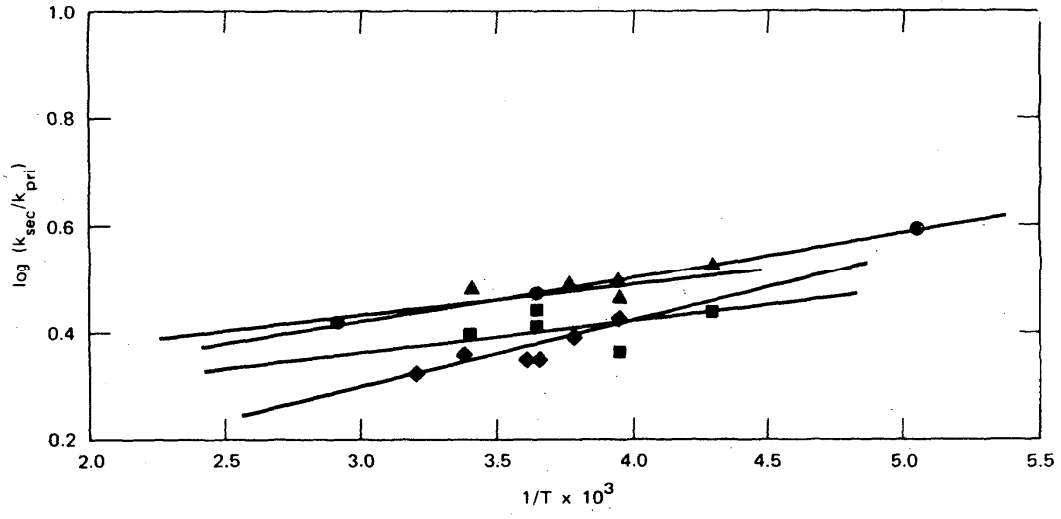

FIGURE 1(a) ARRHENIUS PLOT OF INTERNAL RELATIVE REACTIVITY OF SECONDARY CH BONDS RELATIVE TO PRIMARY CH BONDS TOWARD CHLORINE ATOM IN NONCOMPLEXING SOLVENT: ● n-BUTANE; ■ n-PENTANE, 2-CARBON; ▲ n-PENTANE, 3-CARBON; ◆ n-OCTANE

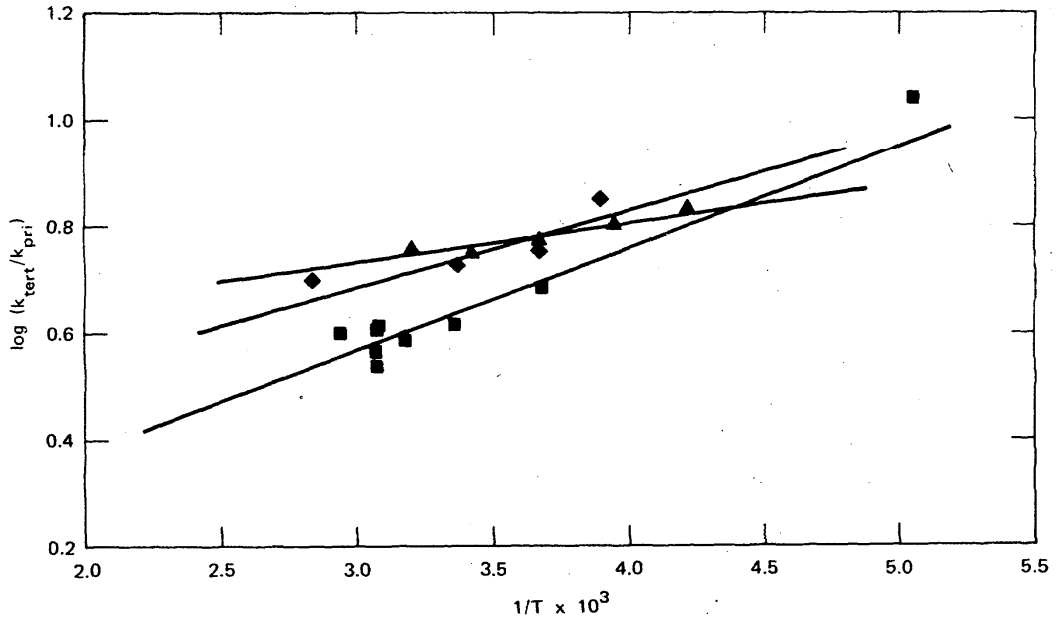

FIGURE 1(b) ARRHENIUS PLOT OF INTERNAL RELATIVE REACTIVITY OF TERTIARY CH BONDS RELATIVE TO PRIMARY CH BONDS TOWARD CHLORINE ATOM IN NONCOMPLEXING SOLVENT: ▲ 2,5-DIMETHYLPENTANE; ■ 2,3-DIMETHYLBUTANE; ◆ TRIMETHYLBUTANE

For reactions of alkanes in complexing solvents such as most aromatic solvents and CS_2 and for reactions of benzylic compounds, the data do not warrant assigning to the ratios A_{tert}/A_{pri} and A_{sec}/A_{pri} values other than unity. Thus

$$\log (A_{tert}/A_{pri}) - \log (A_{sec}/A_{pri}) = 0.$$

The uncertainty in this ratio is ± 0.3.

Table 2.1 summarizes the reactivity for the various positions in representative compounds compared with the aliphatic primary C–H bond in 2,3-dimethylbutane in noncomplexing solvents. If there were some absolute rate data in solution, these relative data could be connected to an absolute basis; however, none is available. The assumption that the absolute rate constants for simple aliphatic compounds are the same in both liquid and gas phases is not valid because it leads to the conclusion that the liquid phase reactions should be diffusion controlled. If this were true, one should find that different, but structurally similar, compounds such as nuclear-substituted toluenes would all react at the same rate, but this is not the case.

2.4. Relative Reactivity Data

The relative reactivity data available are summarized in tables 2.2 through 2.7 by substrate on a per hydrogen basis as defined in section 2.1. Names of compounds follow CA usage. The reactive position is indicated by carbon number, following IUPAC convention for numbering except for arylalkanes where Greek numerals are used for sidechain carbons. Relative rate constants are unitless.

We report solvent compositions for many chlorine atom reactions either in mole percent or molar units, following the original reports. Compositions reported

TABLE 2.1. Chlorine atom-organic compounds: summary of relative reactivities in noncomplexing solvents relative to the primary position of 2,3-dimethylbutane at 313 K per reactive hydrogen (summarized from tables 2.2–2.7)

Compound	Position	k/k_{pri}	$\log A/A^c_{pri}$	$-(E-E_{pri})$ (kJ/mol)	(kcal/mol)
Butane [a]	2	2.8	0.15	1.8	(0.44)
Isobutane [a]	2	3.2	0.15	2.2	(0.52)
2,3-Dimethylbutane	1	1.0	0.0	0.0	(0.0)
	2	3.9	0.15	2.7	(0.65)
Pentane [a]	2	2.4	0.15	1.4	(0.33)
Neopentane	1	1.41	0.0	0.92	(0.22)
Tetramethylsilane	1	1.09	0.0	0.17	(0.04)
2,2-Dichloropropane	1	0.037	0.0	−8.6	(−2.06)
1-Chlorohexane	1	0.19	0.0	−4.3	(−1.03)
	2	0.86	0.15	−1.3	(−0.32)
	3	1.26	0.15	−0.33	(−0.08)
	4	2.11	0.15	1.0	(0.24)
	5	2.04	0.15	0.92	(0.22)
	6	0.96	0.0	−0.13	(−0.03)
1-Acetoxypentane	1	0.37	0.0	−2.6	(−0.63)
	2	1.02	0.15	−1.0	(−0.25)
	3	2.4	0.15	1.3	(0.32)
	4	2.8	0.15	1.8	(0.43)
	5	1.0	0.0	0.0	(0.0)
Cyclopropane		0.22	0.15	−5.0	(−1.2)
Cyclobutane		1.7	0.15	0.50	(0.12)
Cyclopentane		2.8	0.15	1.8	(0.43)
Cyclohexane		2.7	0.15	1.7	(0.40)
Cycloheptane		3.0	0.15	2.0	(0.47)
Cyclooctane		4.3	0.15	2.9	(0.69)
Toluene [b]	α	1.15	0.0	0.36	(0.09)
Ethylbenzene [b]	α	3.5	0.15	2.4	(0.56)
	β	1.8	0.00	1.6	(0.37)
Cumene [b]	α	7.8	0.15	4.4	(1.05)
	β	2.2	0.0	2.0	(0.49)
Diphenylmethane [b]	α	2.7	0.15	1.7	(0.40)
Triphenylmethane [b]	α	10.0	0.15	5.0	(1.2)
1-Phenylcyclopentane [b]	α	13.0	0.15	5.8	(1.4)
1-Phenylcyclohexane [b]	α	9.9	0.15	5.0	(1.2)
trans-2-Butene	1	1.86	0.15	0.154	(0.037)

[a] Reactivity of 1 position assumed to equal 1 position of 2,3-dimethylbutane.

[b] Reactivity at infinite dilution in $C_6H_5NO_2$ or CCl_4.

[c] Evaluated from plots of $\log(k/k_{pri})$ versus $1/T$ for selected compounds; see figure 1.

TABLE 2.2. Cl atom-alkanes: relative reactivity per reactive hydrogen

Substrate and position	Standard	Solvent	Temp., K	k/k_s	Reference
Isobutane 2-CH	1-CH	Reactant	258	4.5	5
			263	3.2	6
		80 mol % CCl_4	263	3.2	
			273	3.4	
		CCl_4	297	3.2	7
		5.9 *M* C_6H_5Cl	258	29.0	5
		80 mol % C_6H_6	273	39.6	6
		80 mol % $CH_3C_6H_5$	273	37.6	
		80 mol % CS_2[a]	253	41.6	
			253	35.8	
			273	28.6	
			283	26.2	
Neopentane 1-CH	2,3-dimethylbutane	4.1 *M* CCl_4	341	1.38	8
	1-CH	4.5 *M* CCl_4	341	1.70, 1.66	
		5.6 *M* C_6H_6	341	1.48	
n-Butane 2-CH	1-CH	Reactant	198	4.00 ± 0.03	8
			273	3.09 ± 0.03	
		$C_6H_5NO_2$	341	2.69 ± 0.08	
		9 *M* C_6H_6	341	5.11	
		11.1 *M* CS_2	273	13.2	
			307	7.8	
			341	6.55	
		13.3 *M* CS_2	273	62.5	
			307	39.6	
	C_6H_{12}	5 *M* CCl_4	273	1.12 ± 0.02	
			341	1.17 ± 0.02	
		7.3 *M* C_6H_6	341	1.28	
2,3-Dimethyl-butane 2-CH	1-CH	Reactant	198	11.0	8
			273	4.96	
			278	4.2	5
			313	3.9	
			328	3.7	5, 4
			341	4.04	8
		CCl_4	298	4.2	9
			313	3.9	
		4.0 *M* CCl_4	328	3.5	5, 4
		4.1 *M* CCl_4	341	3.7	8
		4.5 *M* CCl_4	341	4.2	
		5.2 *M* CCl_4	341	4.1	
		4.0 *M* C_6H_5Cl	298	17.1	5
			313	13.5	
			328	10.2	
		2.0 *M* C_6H_6	278	11.0	
			313	8.6	
			328	8.0	
		4.0 *M* C_6H_6	298	20.0	
			313	17.0	
			328	14.6	
		8.0 *M* C_6H_6	298	49.0	
2,3-Dimethylbutane 2-CH	1-CH	Reactant	313	40.0	
			328	32.0	
		4.0 *M* $tBuC_6H_5$	298	35.0	
			328	24.0	
		11.1 *M* CS_2	273	93.2	8
			307	51.4	
			341	34.0	
		CCl_4	313	1.44	5, 10
		4 *M* C_6H_6	313	3.3	
		4 *M* $tBuC_6H_5$	313	4.3	
		12 *M* CS_2	313	10.0	
1-CH	C_6H_{12}	CCl_4	313	0.37	
		4 *M* C_6H_6	313	0.19	
		4 *M* t-BuC_6H_5	313	0.145	
		12 *M* CS_2	313	0.05	
2,2,3-Trimethylbutane 3-CH	4-CH	Reactants	258	4.5 ± 0.2	11

TABLE 2.2. Cl atom-alkanes: relative reactivity per reactive hydrogen—Continued

Substrate and position	Standard	Solvent	Temp., K	k/k_s	Reference
			273	3.7	
			298	3.4	
			353	3.2	
n-Pentane 2-CH	1-CH		233	2.86	6
			253	2.38	
n-Pentane 2-CH	1-CH		273	2.80	6
			293	2.55	
		80% CCl_4	273	2.62	
		C_6H_6	273	15.18	
			283	11.75	
			293	9.97	
			306	7.51	
			323	7.25	
		80 mol % CS_2[b]	253	14.49	
			273	10.76	
			283	10.37	
			293	9.51	
			306	5.94	
		CS_2	203	22.5	12
			253	9.0	
3-CH	1-CH	Reactant	233	3.42	6
			253	3.22	
			273	3.16	
			293	3.08	
		80% CCl_4	273	2.98	
		80% C_6H_6	273	17.48	
			283	14.03	
			293	11.14	
			306	9.48	
			323	8.58	
n-Pentane 3-CH	1-CH	80% CS_2	253	21.58	15
			273	15.48	
			283	13.76	
			293	12.06	
			306	7.19	
3-CH	2-CH	Reactants	293	1.09	13
		C_6H_6	293	1.31	
1-CH	2,3-Dimethyl butane 1-CH	CCl_4	298	0.97	9
		4 *M* C_6H_6		0.97	
		4 *M* t-BuC_6H_5		0.92	
		12 *M* CS_2		0.86	
2,2,4-Trimethylpentane	C_6H_{12}	CCl_4	313	1.19	10
		4 *M* C_6H_6		1.62	
3-CH[c]		12 *M* CS_2		1.28	
4-CH		CCl_4		0.53	
		4 *M* C_6H_6		0.75	
		12 *M* CS_2		1.09	
5-CH		CCl_4		0.44	
		4 *M* C_6H_6		0.27	
		12 *M* CS_2		0.064	
2,3,4-Trimethylpentane 2-CH	1-CH	Reactant	293	2.41	14
3-CH			293	4.23	
3-CH_3			293	0.85	
2,2,4,4-Tetramethylpentane	C_6H_{12}	CCl_4	313	0.34	10
1-CH		4 *M* C_6H_6	313	0.11	
3-CH		CCl_4	313	0.68	15
		4 *M* C_6H_6	313	0.91	
3,3-Diethylpentane	1-CH	Reactant	293	2.01	8
2-CH					
n-Hexane	1-CH	33% CCl_4	203	3.53	16
Ave. 2,3-CH					

TABLE 2.2. Cl atom-alkanes: relative reactivity per reactive hydrogen—Continued

Substrate and position	Standard	Solvent	Temp., K	k/k_s	Reference
			240	2.86	
			258	2.52	
			276	2.26	
			273	2.29	
			295	2.31	
			312	2.41	
2-CH		Reactant	293	2.45 ± 0.13	17
3-CH			293	2.65 ± 0.13	
2,5-Dimethyl-hexane	1-CH		238	4.34 ± 0.21	15
2-CH			254	4.07 ± 0.04	
			273	3.85 ± 0.13	
			293	3.60 ± 0.12	
2,5-Dimethyl-hexane 2-CH	1-CH		313	3.65 ± 0.10	15
			333	3.56 ± 0.09	
		4 *M* C_6H_6[d]	273	13.5 ± 0.4	
			293	11.2 ± 0.2	
			313	9.0 ± 0.05	
			333	7.69 ± 0.47	
		6 *M* C_6H_5F	238	26.8 ± 1.6	
			254	22.4 ± 0.5	
			273	16.5 ± 0.3	
			293	14.1 ± 1.0	
			313	11.1 ± 0.5	
			333	9.75 ± 0.2	
		12 *M* CS_2	283	75 ± 5	
			293	75 ± 9	
			313	46 ± 3	
3-CH	1-CH	Reactant	238	2.77 ± 0.09	
			254	2.80 ± 0.04	
			273	2.75 ± 0.07	
			293	2.68 ± 0.12	
			313	2.65 ± 0.05	
			333	2.60 ± 0.08	
		4 *M* C_6H_6[a]	273	4.60 ± 0.10	
			293	4.31 ± 0.09	
			313	3.91 ± 0.03	
			333	3.54 ± 0.21	
2,5-Dimethylhexane, 2-CH	1-CH	4 *M* C_6H_6[d]	273	4.60 ± 0.10	15
			293	4.31 ± 0.09	
			313	3.91 ± 0.03	
			333	3.54 ± 0.21	
		6 *M* C_6H_5F	238	7.04 ± 0.26	
			254	6.46 ± 0.18	
			273	5.61 ± 0.10	
			293	5.24 ± 0.32	
			313	4.80 ± 0.20	
			333	4.62 ± 0.13	
		12 *M* CS_2	283	16 ± 1	
			293	16 ± 2	
			313	11.7 ± 0.8	
1-CH	C_6H_{12}	CCl_4	313	0.33	18
		6 *M* C_6H_6		0.15	
		6 *M* C_6H_5F		0.17	
		12 *M* CS_2		0.068	
2-CH	C_6H_{12}	CCl_4		1.20	
		6 *M* C_6H_6		2.30	
		6 *M* C_6H_5F		1.89	
		12 *M* CS_2		3.13	
3-CH	C_6H_{12}	CCl_4		0.87	
		6 *M* C_6H_6		0.78	
		6 *M* C_6H_5F		0.82	
		12 *M* CS_2		0.80	
3,4-Dimethylhexane, 3-CH_3	1-CH	Reactant	293	0.8	14
n-Heptane 2-CH	1-CH	Reactant	288	2.88	19

TABLE 2.2. Cl atom-alkanes: relative reactivity per reactive hydrogen—Continued

Substrate and position	Standard	Solvent	Temp., K	k/k_s	Reference
			293	3.54	20
			313	2.53	19
			328	3.5	21
			353	2.11	19
3-CH	1-CH		288	2.67	19
			293	3.35	20
			313	2.26	19
			328	3.4	21
			353	1.93	19
4-CH	1-CH		288	2.65	19
			293	3.34	20
			313	2.34	19
			328	3.2	21
			353	1.79	19
3-CH	2-CH		293	0.96	13
		C_6H_6	293	1.18	13
2-Methylheptane	1-CH	Reactant	293	2.90	14
2-CH					
3-CH			293	2.64	
4-CH			293	1.77	
5-CH			293 }	Average	
6-CH			293 }	2.56	
7-CH			293	1.22	
3-Methylheptane	1-CH		293	0.8	14
$3\text{-}CH_3$					
n-Octane	1-CH	Reactant	253	3.23	20
2-CH					
			293	3.19	20
			293	2.15 ± 0.11	17
3-CH			253	3.02	20
			293	2.98	20
			293	2.20 ± 0.11	17
4-CH			253	2.72	20
			293	2.80	20
			293	2.20 ± 0.11	17
n-Decane	1-CH		263	2.72	
2-CH					
			293	2.74	
			371	2.68	
3-CH			263	2.64	
			293	2.66	
			371	2.66	
4-CH			263	2.66	
			293	2.52	
			371	2.59	
5-CH			263	2.50	
			293	2.48	
			371	2.56	

[a] Data at various CS_2 concentrations.
[b] Data at various CS_2 concentrations in both references 6 and 12.
[c] Additional data in reference 6.
[d] Additional data at 6 and 8 *M* solvent.

TABLE 2.3. Chlorine atom-cycloalkanes: relative reactivities per reactive hydrogen

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Cyclopropane	C_6H_{12}	5 *M* CCl_4	273	0.048	22
			341	0.100	
		7.3 *M* C_6H_6	341	0.136	
Cyclobutane	C_6H_{12}	5 *M* CCl_4	273	0.84	22
			341	0.67	
		7.3 *M* C_6H_6	341	0.76	
Cyclopentane	C_6H_{12}	5 *M* CCl_4	273	0.95	22
			341	0.85	
	2,3-Dimethylbutane 1-CH	CCl_4	313	2.8	9
		4 *M* C_6H_6	313	5.2	
		4 *M* t-BuPh	313	7.3	
		12 *M* CS_2	313	23.	
Cyclohexane	2,3-Dimethylbutane 1-CH	CCl_4	313	2.7	9
		4 *M* C_6H_6	313	5.2	
		4 *M* t-BuPh	313	6.9	
		12 *M* CS_2	313	20.	
		5.2 *M* CCl_4	341	2.1	8
		4.5 *M* CCl_4	341	1.94	
		5.6 *M* C_6H_6	341	5.8	
Cycloheptane	2,3-Dimethylbutane 1-CH	CCl_4	313	3.0	9
		4 *M* C_6H_6	313	6.4	
		4 *M* t-BuPh	313	10.	
		12 *M* CS_2	313	40.	
Cyclooctane	2,3-Dimethylbutane 1-CH	CCl_4	313	4.3	9
		4 *M* C_6H_6		9.2	
		4 *M* t-BuC_6H_5		16.	
		12 *M* CS_2		75.	
Bicyclo(2.1.1)hexane 2-CH	C_6H_{12}	CCl_4	298	2.4	23
Bicyclo(2.2.1)heptane 2-CH	C_6H_{12}	5 *M* CCl_4	341	1.04±0.05	8
		CCl_4	273	0.99±0.05	24
		CCl_4	353	0.79±0.03	
1-CH	C_6H_{12}	CCl_4	313	1.43±0.27	
		4 *M* C_6H_6		3.52±0.63	
		12 *M* CS_2		6.94±1.9	
Adamantane[a]	C_6H_{12}	CCl_4	313	0.65±0.07	15
		4 *M* C_6H_6		1.04±0.17	
		12 *M* CS_2		1.42±0.37	

[a] Adamantane is tricyclo [3.3.1.$1^{3,7}$] decane.

TABLE 2.4. Chlorine atom-arylakanes and allylic compounds: relative reactivities per reactive hydrogen

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Toluene	2,3-Dimethylbutane 1-CH	CCl_4	313	1.15	9
		4 *M* C_6H_6	313	2.1	
		4 *M* t-BuPh	313	2.8	
		12 *M* CS_2	313	11.	
Toluene, 2 *M*	C_6H_{12}	Reactants	313	0.4	
4 *M*			313	0.36	
8 *M*			313	0.35	
			298	0.37	
			328	0.40	
	$PhCH_2D$ α-CD		353	2.0	19
			343	2.1	25
		CCl_4	350	1.3	26
		Reactants	383	1.5	
	C_6H_{12}		353	0.36	27
	2,3-Dimethylbutane 1-CH	$C_6H_5NO_2$	313	1.4	28
m-Xylene	Toluene α-CH	CCl_4	313	1.30 ± 0.02	29
p-Xylene			313	1.57 ± 0.01	
m-Chlorotoluene			313	0.595 ± 0.005	
p-Chlorotoluene			313	0.79 ± 0.01	
		C_6H_6	313	0.79 ± 0.01	
	p-$ClC_6H_5CH_2D$ α-CD	CCl_4	313	1.44 ± 0.08	
p-Nitrotoluene	Toluene α-CH		313	0.32 ± 0.01	
p-Phenyltoluene	Toluene α-CH	CCl_4	313	1.55 ± 0.01	29
m-Phenoxytoluene	Toluene α-CH	CCl_4	313	0.86 ± 0.01	
p-Phenoxytoluene	Toluene α-CH	CCl_4	313	2.50 ± 0.02	
Ethylbenzene α-CH	2,3-Dimethylbutane 1-CH	$C_6H_5NO_2$	313	3.5	28
β-CH			313	1.8	
Cumene α-CH	2,3-Dimethylbutane 1-CH	CCl_4 [a]	313	7.8	
β-CH			313	2.2	
n-Propylbenzene [a]					30
n-Butylbenzene α-CH	n-Butylbenzene, α-CH	CCl_4	313	5.9	28
β-CH			313	2.7	
γ-CH			313	4.0	
Iso-butylbenzene α-CH		Reactant	293	14.8	30
β-CH_3			293	1.1	
β-CH_2			293	2.1	
t-Butylbenzene	2,3-Dimethylbutane 1-CH	CCl_4	313	0.63	9, 28
		4 *M* t-BuPh	313	0.60	
	Toluene α-CH	Reactant	353	0.22	
Indan α-CH	2,3-Dimethylbutane 1-CH	$C_6H_5NO_2$	313	6.1	28
β-CH			313	4.7	
Tetralin α-CH	2,3-Dimethylbutane 1-CH		313	5.8	
β-CH			313	5.5	
Diphenylmethane sec-CH	2,3-Dimethylbutane 1-CH	$C_6H_5NO_2$	313	2.7	28
Triphenylmethane tert-CH			313	10.	
Phenylcyclopentane tert-CH			313	13.	
Phenylcyclohexane tert-CH			313	9.9	
		Allylic compounds			
trans-2-Butene 1-CH	C_6H_{12}	Reactants	273	0.69	31
cis-2-Butene 1-CH			273	0.60	31
1-Butene 3-CH			273	0.76	31
Cyclohexene 3-CH			273	1.20	32
1-Butyne 3-CH			273	0.27	32

[a] Reactivity data measured neat can be found in references 6 and 30.

TABLE 2.5. Chlorine atom-haloalkanes: relative reactivity per reactive hydrogen

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Dichloromethane	2,3-Dimethylbutane	CCl_4	313	0.011	9
	1-CH	4 *M* t-BuC_6H_5	313	0.030	
		12 *M* CS_2	313	0.044	
Trichloromethane		CCl_4	313	0.0051	9
		4 *M* t-BuC_6H_5	313	0.017	
		12 *M* CS_2	313	0.033	
1-Chloroethane					8
1-CH	2-CH	6.9 *M* CCl_4	273	3.2	
		7.6 *M* C_6H_6	273	7.2	
		6.6 *M* C_6H_5Cl	273	5.6	
		11.1 *M* CS_2	273	8.2	
1-Chloroethane	2,2-Dichloropropane	Reactants	313[a]	8.3	33
1-CH					
2-CH				2.3	
1,1-Dichloroethane	2-CH	Reactants	291–318	10.	34
1-CH		8 *M* CS_2	291–318	17–27	
1,1-Dichloroethane	2,2 Dichloropropane				
2-CH			313	0.6	
1-CH			313	4.7	
$CH_3CCl_2CH_3$	Tetraethylmethane 1-CH	Reactants	313	0.037	35
1,1-Dichloro-2,2-difluoroethane	2-CH		338 ± 5	1.31	36
1-CH					
Trichloroethane	2,2-Dichloropropane		313	0.07	33
1,2-Dichloroethane			313	3.0	
1,1,2-Trichloroethane					
1-CH			313	0.78	
2-CH			313	0.47	
1,1,1,2-Tetrachloroethane	2,2-Dichloropropane	Reactants		0.24	33
1,1,2,2-Tetrachloroethane				0.43	33
1,1,1,2,2-Pentachloroethane				0.44	33
1-Chloropropane 1-CH	3-CH	Reactants	333	0.82	37
		CCl_4	313	0.57	38
			298	0.8	39
			319	0.8	39
2-CH			333	2.2	37
		CCl_4	313	2.8	38
			293	2.6	39
			319	2.3	39
	2,2-Dichloropropane		313	58	40
3-CH			313	21	40
1-Chloro-2-methylpropane					
1-CH	$(CH_3)_3CH$	CCl_4	297	0.43	7
2-CH			297	2.63	
3-CH			297	0.58	
1-CH	$(CH_3)_3CCl$	CCl_4	297	1.78	41
2-CH			297	8.02	
3-CH			297	2.25	
1-CH		5 *M* C_6H_6/CCl_4	297	2.50	
2-CH			297	31.2	
3-CH			297	1.98	
1-CH		CS_2	297	3.94	
2-CH			297	60.3	
3-CH			297	1.98	
1,1-Dichloropropane 2-CH	2,2-Dichloropropane	Reactants	313	14	40
3-CH			313	11	40
1-CH			313	0.32	37
2-CH	3-CH		358	1.4	37
1,3-Dichloropropane 1-CH	2-CH		358	0.75	37
1,1,1-Trichloropropane 2-CH	3-CH		358	1.1	42
1,1,3-Trichloropropane					
1-CH	3-CH		358	0.9	42
3-CH			358	1.4	42
1,2,3-Trichloropropane 1-CH	2-CH		293[b]	0.4	43
1,2,2-Dichloropropane 1-CH	3-H		358	3.2	43
1-Chloro-2,2-difluoropropane 1-CH	2,2-Difluoropropane		318	4.1	44

TABLE 2.5. Chlorine atom-haloalkanes: relative reactivity per reactive hydrogen—Continued

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
1-Chloro-2,2-difluoropropane 3-CH		CCl_4	318	0.11	
1,1,1-Trichloro-2,2-difluoropropane			318	0.12	
1,3-Dichloro-2,2-difluoropropane			318	1.1	
1,1,1,3-Tetrachloro-2,2-difluoropropane	2,2-Difluoropropane	Reactant	318	1.2	44
1,1-Dichloro-2,2-difluoropropane					
1-CH			318	4.4	
1,1,1,3,3-pentachloro-2,2-difluoropropane			318	1.3	
$(CH_3)_3CCl$	$(CH_3)_3CH$	CCl_4	297	0.24	7
$(CH_3)_3CCl$	2,2-Dichloropropane		313	9.8	35
1-Chloro-2,2-dimethylpropane	3,3-Dichloropropane		313	20	40
1-CH				20	
2-Chloro-2-methylbutane	2,2-Dichloropropane				
3-CH			313	90	40
4-CH			313	25	40
1-Chlorobutane [c]					
1-CH	4-CH		307	0.5 [d]	8
2-CH				1.9 [e]	
3-CH				4.2 [f]	
1,1-Dichlorobutane	4-CH	SO_2Cl_2/CCl_4			
1-CH			353	0.08	45
2-CH				0.5	
3-CH				1.9	
1-CH			353	0.12	39
2-CH				0.4	
3-CH				1.8	
2,2-Dichlorobutane					
3-CH	2,2-Dichloropropane		313	26	40
4-CH			313	15	40
1,2,2-Trichloro-3-methylbutane	2,2-Dichloropropane	Reactant			
4-CH			313	3.4	34
1-CH			313	5.9	34
3-Chloro-3-ethyl pentane					
4-CH			313	19	40
5-CH			313	9.3	40
3,3-Dichloropentane	2,2-Dichloropropane	Reactants			
4-CH			313	7.2	40
5-CH			313	4.4	40
1,1,1-Trichlorobutane	3-CH	SO_2Cl_2/CCl_4			
1-CH				0.2	45
2-CH				1.3	
1-Chlorohexane	n-Hexane 1-CH		293		
1-CH				0.16	17
2-CH				0.83	
3-CH				1.24	
4-CH				2.17	
5-CH				2.10	
6-CH				0.95	
1-CH	6-CH		353	0.3	39
2-CH				0.9	
3-CH				2.0	
4-CH				2.9	
5-CH				2.9	
2-Chlorohexane	n-Hexane 1-CH	Reactants	293		17
1-CH				0.05	
2-CH				0.29	
3-CH				0.90	
4-CH				1.16	
5-CH				1.42	
6-CH				0.68	
3-Chlorohexane	n-Hexane 1-CH		293		17
1-CH				0.18	
2-CH				0.66	
3-CH				0.42	
4-CH				0.51	
5-CH				0.90	

TABLE 2.5. Chlorine atom-haloalkanes: relative reactivity per reactive hydrogen—Continued

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
6-CH				0.32	
1,1-Dichlorohexane	6-CH		253		39
1-CH				~0	
2-CH				0.4	
3-CH				0.9	
4-CH				2.6	
5-CH				3.1	
1,2-Dichlorohexane	6-CH		253		39
1-CH				0.4	
2-CH				0.8	
3-CH				0.9	
4-CH				0.9	
5-CH				3.3	
1-Chlorooctane[g]	n-Octane 1-CH				
1-CH			293	0.18	17
2-CH				0.66	
3-CH				0.42	
4-CH				0.51	
5-CH				0.90	
6-CH				0.32	
1-Chlorocyclopentane[h]					
1-CH	C_6H_{12}	CCl_4	313	0.21	46
2-CH				0.37	
3-CH				0.75	
1-CH		CCl_4	243	0.18	
2-CH				0.32	
3-CH				0.75	
1-Chlorocyclohexane[i]					
1-CH		CCl_4	313	0.36	47
2-CH				0.44	
3-CH				0.79	
1-Bromocyclohexane					
1-CH	4-CH	CCl_4	313	0.40	47
2-CH				0.20	
3-CH				0.91	
1-CH			243	0.17	
2-CH				0.20	
3-CH				0.62	
1-CH		CS_2		0.36	
2-CH				0.24	
3-CH				0.59	

[a] Relative reaction rates at 293 K found in reference 33.
[b] Relative reaction rates at 358 and 423 K can be found in reference 43.
[c] Data available using C_6H_6 and CS_2 as solvents as well, references 8 and 39.
[d] $\Delta E_a = -0.37 \pm 0.23$, $\log (A/A_a) = -0.03 \pm 0.15$.
[e] $\Delta E_a = 0.23 \pm 0.09$, $\log (A/A_a) = 0.11 \pm 0.06$.
[f] $\Delta E_a = 0.50 \pm 0.09$, $\log (A/A_a) = 0.26 \pm 0.06$.
[g] Relative reaction rates at 253 K can be found in reference 39.
[h] Reaction rates measured in CH_3CN, $PhNO_2$, C_6H_6, Ph_2O, and CS_2 can be found in reference 46.
[i] Further information on chlorocyclohexane can be found in reference 48.

TABLE 2.6. Chlorine atom-silane: relative reactivity per reactive H

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Tetramethylsilane	2,3-Dimethylbutane 1-CH	CCl_4	298	1.1	9
		4 *M* t-BuC_6H_5	298	1.1	9
		12 *M* CS_2	298	0.16	9
	Tetraethylmethane 1-CH	Reactants	313	4.36	35
Chlorotrimethylsilane	2,3-Dimethylbutane 1-CH	CCl_4	313	0.17	9
		4 *M* C_6H_6	313	0.16	
		4 *M* t-BuC_6H_5	313	0.16	
		12 *M* CS_2	313	0.20	
	Tetraethylmethane 1-CH	Reactants	313	0.45	35
Methyltrichlorosilane			313	0.0048	
Dichlorodimethylsilane			313	0.045	
Chloromethyl-methyldichlorosilane			313	0.24	
Chloromethyldimethylchlorosilane 1-CH_3			313	0.16	
1-CH_2Cl			313	0.89	
Chloromethyltrimethylsilane 1-CH_3			313	0.81	
1-CH_2Cl			313	2.2	
Tetraethylsilane α-CH			313	1.5	
β-CH			313	2.4	
Dichlorodiethylsilane α-CH			313	0.78	
β-CH			313	0.89	
Ethyltrichlorosilane α-CH			313	0.45	
β-CH			313	0.28	

TABLE 2.7. Chlorine atoms-miscellaneous compounds: relative reactivity per reactive H

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Pentanoyl chloride					
2-CH	4-CH	Reactants	293	0.8	13
3-CH			293	2.5	
Acetoxybutane					
1-CH	4-CH		298	0.3	49
2-CH			298	1.2	
3-CH			298	2.5	
Trichloroacetoxybutane					
2-CH	4-CH		253	0.14	13
3-CH			353	1.1	
Butanesulfonyl chloride					
2-CH	4-CH		353	0.007	39
3-CH			353	0.85	
Hexanoyl chloride [a]					
2-CH	5-CH		293	0.6	13
3-CH			293	2.0	
4-CH			293	2.8	
Acetoxypentane					
1-CH	5-CH		300	0.3	49
2-CH			300	1.0	
3-CH			300	2.5	
4-CH			300	2.9	
Heptanoyl chloride					
1-CH	6-CH	CH_3CN	325	0.06	50
2-CH			325	0.4	
3-CH			325	0.9	
4-CH			325	1.1	
5-CH			325	1.4	
Trichloroacetoxyhexane					
3-CH	6-CH	Reactants	353	0.18	39
4-CH			353	2.2	
5-CH			353	3.1	
Octanoyl Chloride [b]					
2-CH	7-CH		293	0.5	13
3-CH			293	1.5	
4-CH			293	2.0	
5-CH			293	2.5	
6-CH			293	2.6	

[a] Data available using the following solvents: C_6H_6, CCl_4 and CH_3CN in references 13 and 50.

[b] Data available using C_6H_6 as solvent in reference 12.

in molar units are temperature dependent and almost always refer to 298 K. Compositions reported in mole percent of one component imply that the reactant(s) is the other component. In some cases the reactant or reactants serve as solvent.

Where reported in the original paper, error limits are included in the tabulation. These error limits are usually estimated as twice the standard deviation (95 percent confidence limits).

References for Section 2

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3. Reactions of Alkyl Radicals

The available information on H-atom transfer reactions of alkyl radicals deals predominantly with methyl radicals. Only a small amount of data for other alkyl radicals exists. Therefore this section covers data on methyl radicals but includes some data on ethyl radicals.

The data that are available, like much of the liquid phase radical data, are relative reactivity data. However by combining data on the photolysis of acetone in solution with rate constants for methyl radical combination in solution along with the relative rate data, it is possible to derive absolute rate constants for H-atom transfer by methyl radicals. The use of similar information for ethyl radical allows only two reactions to be put on an absolute basis.

3.1. Relative Rate Data for Methyl Radical

There are four basically different ways by which relative reactivity toward methyl radicals has been determined. The first involves generating methyl radicals, generally by decomposing acetyl peroxide, in the presence of the desired hydrogen atom donor and carbon tetrachloride.

$$CH_3C(=O)OC(=O)CH_3 \longrightarrow 2CH_3\cdot + 2CO_2 \qquad (1)$$

$$CH_3\cdot + RH \xrightarrow{k_H} CH_4 + R\cdot \qquad (2)$$

$$CH_3\cdot + CCl_4 \xrightarrow{k_{Cl}} CH_3Cl + CCl_3\cdot \qquad (3)$$

By measuring the ratio of CH_4 and CH_3Cl one may obtain the desired relative reactivity

$$d[CH_4]/d[CH_3Cl] = (k_H/k_{Cl})\ [RH]/[CCl_4], \quad (4)$$

$$k_H/k_{Cl} = [CH_4][CCl_4]/[CH_3Cl][RH].$$

This method was first used by Edwards and Mayo [1] but only with the work of Pryor et al. [2] did it become apparent that the procedure had some limitations. Complications arise using this technique if the hydrogen-donating substrate can readily chlorinate via the reactions

$$CCl_3\cdot + RH \longrightarrow CCl_3H + R\cdot \quad (5)$$

$$R\cdot + CCl_4 \longrightarrow RCl + CCl_3\cdot \quad (6)$$

Small contributions by these reactions do not interfere with the methyl radical reactivity determinations since no CH_4 or CH_3Cl is formed in the sequence. However, reactions (5) and (6) do deplete both RH and CCl_4, thereby affecting the calculation of k_H/k_{Cl} since the concentrations of RH and CCl_4 are used in eq (4). In addition, CCl_3H has a higher reactivity than CCl_4 toward Cl-abstraction; thus the formation of CCl_3H in reaction (5) adds the possibility of an additional route to CH_3Cl formation

$$CH_3\cdot + CCl_3H \longrightarrow CH_3Cl + CCl_2H\cdot \quad (7)$$

Pryor et al. [2] have shown that this technique generally gives reliable data for aralkanes and presumably for various alkenes where the resonance-stabilized radical formed by hydrogen abstraction is too unreactive to undergo reaction (6) relative to termination reactions.

However, for alkanes where reaction (5) is considerably exothermic reactions (4) and (5) are important and sufficient to make the measured values of k_H/k_{Cl} invalid at the conversion generally encountered. Thus this technique is satisfactory for aralkanes but not alkanes. It would appear that if a suitable solvent were available to lower the concentrations of RH and CCl_4, its use could reduce and possibly eliminate reactions (4) and (5) and thereby make this technique suitable for alkanes also.

A second technique developed and used by Swarzc and coworkers [3] is largely the outgrowth of an effort to measure rate of addition of methyl radical to olefinic substrates relative to abstraction of hydrogen from isooctane.

$$CH_3\cdot + \text{isooctane} \xrightarrow{k_8} CH_4 + R\cdot \quad (8)$$

$$CH_3\cdot + \text{olefin} \xrightarrow{k_9} \text{Adduct} \quad (9)$$

$$CH_3\cdot + \text{olefin (RH)} \xrightarrow{k_{10}} CH_4 + R'\cdot \quad (10)$$

By comparing methane formed in mixtures of olefin and isooctane, $[CH_4]$, to that formed only in isooctane, $[CH_4]_i$, one obtains

$$[CH_4]/([CH_4]_i - [CH_4]) = (k_8/k_9)$$

$$[\text{isooctane}]/[RH] + k_{10}/k_9. \quad (11)$$

Thus a plot of the left-hand ratio in eq (11) against [isooctane]/[RH] gives k_{10}/k_9 as the intercept and k_8/k_9 as the slope, the ratio of which gives k_{10}/k_8. The more common technique has been to ignore the last term in eq (11); then if the apparent value of k_8/k_9 changes with olefin concentration, a plot of the apparent k_8/k_9 against the ratio [RH]/[isooctane] is made. In this case the intercept gives the true value of k_8/k_9 and the slope gives k_{10}/k_9.

This procedure is invalid if the substrate does not add methyl radical. In such cases the abstraction may be measured relative to addition to a standard compound or compounds [4].

$$CH_3\cdot + S \longrightarrow CH_3-S\cdot \quad (12)$$

The standard in this case has been 1,1-diphenylethylene or trans-stilbene. Thus the formation of methane from decomposition of acetyl peroxide in the presence of a hydrogen donor (RH) and diphenylethylene may be expressed

$$[CH_4]/([CH_4]_i - [CH_4]) = (k_{10}/k_{12})\ [RH]/[S], \quad (13)$$

where $[CH_4]_i$ is the methane formed in absence of S, equal approximately to two times the acetyl peroxide decomposed.

This general technique for comparing H-atom transfer to radical addition has generally given what appear to be satisfactory data. However, for the technique to be totally valid, methyl radicals must react only with the starting reactants. Errors [3] may occur to the extent that methyl radicals react with radicals formed in reactions (8)–(10), (12) and (13), although this factor could be important in only a few cases.

One of the largest potential sources of error arises from formation of radical products that are more reactive than the initial substrate; for example, olefins formed by radical disproportionation are generally more reactive than the initial substrate. This effect is probably largest for alkanes having tertiary hydrogen since tertiary alkyl radicals tend predominately to disproportionate, forming reactive olefins. Some correction for this effect may be made by comparing methane formed in the presence and absence of the olefin that adds radicals. Experiments designed to proceed only to low conversions would minimize this possible complication.

A third approach to evaluating the relative reactivity of methyl radicals involves using a tritium labeled standard (ST) [5, 6].

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \quad (14)$$

$$CH_3\cdot + ST \longrightarrow CH_3T + S\cdot \quad (15)$$

The kinetics can be expressed in terms of the specific activity, A, of the gases formed in mixtures of RH and ST relative to the specific activity, A_0, of gas formed in the absence RH.

$$\frac{A_0 - A}{A} = (k_{14}/k_{15})\,(\mathrm{RH/ST}).$$

Thus, while similar in some respects to the previous technique, it is undoubtedly more accurate because of the precision with which specific activity can be measured. This technique does away with the problem associated with addition to double bonds of the substrate or standard. Reactions need be carried only to low conversions where reactions of the initial products are unimportant.

The precision and presumably the accuracy of this technique appears to be in the range of ±5 percent as judged from the reported standard deviations. This compares with values of ±10 percent for the previous technique for generally larger samples. There have been cases where observed relative reactivities are sensitive to the proportion of reactants. These effects may be true media effects but more than likely are the result of complicating side reactions of the type discussed above. Until this problem is resolved, some factor of uncertainty of 2 to 3 must be associated with all the previous techniques.

Pryor et al. [7] have more recently measured reactivity of a wide variety of compounds toward methyl radical relative to partially deuterated t-butyl mercaptan-S-D at 383 K using t-butyl peracetate as a methyl radical source. The reactions are

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}O_2C(CH_3)_3} \longrightarrow \mathrm{CH_3\overset{O}{\overset{\|}{C}}O\cdot} + \cdot\mathrm{OC(CH_3)} \quad (17)$$

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}O\cdot} \longrightarrow \mathrm{CH_3\cdot} + \mathrm{CO_2} \quad (18)$$

$$\mathrm{CH_3\cdot} + \mathrm{RH} \longrightarrow \mathrm{CH_4} + \mathrm{R\cdot} \quad (19)$$

$$\mathrm{CH_3\cdot} + \text{t-BuSD} \longrightarrow \mathrm{CH_3D} + \text{t-BuS}\cdot \quad (20)$$

$$\mathrm{CH_3\cdot} + \text{t-BuSH} \longrightarrow \mathrm{CH_4} + \text{t-BuS}\cdot \quad (21)$$

The ratio of CH_4-to-CH_3D becomes a measure of the relative reactivity.

$$d[\mathrm{CH_4}]/d[\mathrm{CH_3D}] = (k_{19}/k_{20})\,[\mathrm{RH}]/[\text{t-BuSD}] + (k_{21}/k_{20})\,[\text{t-BuSH}]/[\text{t-BuSD}]. \quad (22)$$

Plots of the ratio of CH_4/CH_3D obtained versus the ratio of [RH]/[t-BuSD] give a line with the slope equal to k_{19}/k_{20} the desired relative reactivity. The intercept is a function of the degree to which the mercaptan is deuterated.

The precision reported is about 15 percent, which is higher than for the other technique. However, the type of complicating reactions discussed for these other techniques do not appear to be important [7]. Therefore the accuracy of this technique is probably about the same as the precision, or ±15 percent. The precision of the data could undoubtedly be improved by evaluating the intercept of the second term on the left-hand side of equation (22) separately. This would require measuring the CH_4/CH_3D ratio in absence of hydrocarbon. Then from one experiment with added hydrocarbon the ratio of k_{19}/k_{20} would be defined and additional experiments would check and define precision.

3.2. Absolute Rate Constants

The pyrolysis of acetone has been studied in neat acetone [8], perfluorodimethylcyclobutane [9], and water [10, 11, 12]. The reactions of methyl radicals formed upon photolysis are

$$\mathrm{CH_3\cdot} + \mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_3} \longrightarrow \mathrm{CH_4} + \cdot\mathrm{CH_2\overset{O}{\overset{\|}{C}}CH_3} \quad (23)$$

$$2\mathrm{CH_3\cdot} \longrightarrow \mathrm{CH_3CH_3} \quad (24)$$

The competition of methane and ethane formation may be expressed

$$\mathrm{R_{CH_4}/R_{C_2H_6}}^{1/2} = (k_{23}/k_{24}^{1/2})\,[\text{acetone}]. \quad (25)$$

At 313 K $k_{23}/k_{24}^{1/2} = 9 \times 10^{-4}\ (M^{-1}\mathrm{s}^{-1})^{1/2}$ in acetone [8], 15×10^{-4} in perfluorodimethylcyclobutane [9], and 3.5×10^{-2} in water, [10, 11, 12]. Since there is little difference in the viscosity of these solvents at 313 K (0.5, 0.7, and 0.7 centipoise, respectively) k_{24} is probably not too different in each solvent and therefore most of the effect must be in k_{23}. The value of k_{24} has been estimated by epr techniques to be $5.5 \pm 0.5 \times 10^9\ M^{-1}\mathrm{s}^{-1}$ in di-t-butyl peroxide solvent at 255 K [13] and $4.5 \times 10^9\ M^{-1}\mathrm{s}^{-1}$ in cyclohexane at 298 K [14]. The average value is $5.0 \pm 1.0 \times 10^9\ M^{-1}\mathrm{s}^{-1}$ independent of temperature. Using this value for k_{24}, the above ratios give k_{23} (in acetone) = $10.6\ M^{-1}\mathrm{s}^{-1}$ per hydrogen and k_{23} (in water) = $412\ M^{-1}\mathrm{s}^{-1}$ per hydrogen at 313 K. An average of eight recent gas phase studies [15 and 16] gives

$$\log k_{23} = 7.72 \pm 0.07 - 9.60 \pm 0.13/\theta;$$

$$\theta = 2.303RT \times 10^{-3}$$

$$k_{23} = 10.4 \pm 0.5 \text{ per C-H bond at 313 K}$$

Thus the liquid phase value of $k = 10.6 \pm 0.5\ M^{-1}$ s per C—H bond obtained in acetone agrees well with the gas phase data. The value in the perfluorinated solvent is

70 per cent larger than the gas phase number. This difference could possibly be due to k_{24} being 2.3 times faster in this solvent as well as a solvent effect on k_{23}.

The results in water are most interesting and, if real, suggest that hydrogen bonding between water and the acetone carbonyl activates the reactivity of the adjacent carbon bonds. However in absence of data for the recombination of methyl radicals in aqueous solution, we cannot be certain that k_{24} is not smaller in water, although the termination constant would have to be an unreasonable 1.5×10^3 times slower in water than in organic solvents to explain the entire difference. Thomas [17] has investigated the reaction of methyl radical in aqueous solution using radiolysis techniques. His rate constant values generally were slightly larger (generally 4–10 times larger) for both addition and abstraction reactions than anticipated by extrapolating gas phase data from a higher temperature. We have not considered reactions in aqueous solutions any further in this review, but it is a research area deserving further study.

Assigning a value for log $(A/M^{-1}s^{-1})$ of 8.0 on a C—H bond basis for acetone which is consistent with recently reported gas phase values for this reaction, the value of k_{23} obtained in acetone can be expressed as

$$\log k(CH_3\cdot + CH_3\overset{\overset{O}{\|}}{C}CH_3) = 8.0 - 9.99/\theta$$

$$\theta = 2.303RT = 4.576T \times 10^{-3}$$

Using this as a primary reference and assuming that it applies in hydrocarbon reaction mixtures, we can evaluate other rate constants that have been compared to acetone. Unfortunately no compounds have been compared directly to acetone. However acetophenone carbon-hydrogen bond is reported to be 2.45 times as reactive at 343 K as a sec C—H bond in n-heptane (table 3.7). Since the α-C—H bond in acetophenone should have the same reactivity as in acetone and assuming log $(A/M^{-1}s^{-1})$ is 9.2 for secondary hydrogen transfer (table 1.1) the Arrhenius expression for reaction of methyl with the secondary position in n-heptane is

$$\log k(CH_3\cdot + \text{sec}-CH) = 9.2 - 12.48/\theta.$$

From this expression, it is possible to evaluate the rate parameters for those compounds that have been measured directly or indirectly, relative to sec-CH position of alkanes using estimated values for log A. Some of these estimated parameters derived largely from data measured relating to t-butyl mercaptan-S-D and to toluene are in table 3.1.

A number of compounds have been measured relative to isooctane. From the data of Pryor et al., it is possible to obtain the Arrhenius expression for reaction for all C—H bonds of this standard.

$$\log k_{iso} = 10.25 - 12.68/\theta \text{ (per molecule)}$$

Thus the absolute value of rate constants reported relative to isooctane may be evaluated by multiplying the relative value by the rate constant for isooctane at the given temperature obtained from this expression. The activation energy then may be calculated by assigning the appropriate A-factor where comparison is possible. The agreement between the values obtained in this manner and those obtained above is within 4 kJ/mol (1 kcal/mol). There are more uncertainties associated with the data based on isooctane and we feel that this approach is less reliable than where comparisons have been based on t-butyl mercaptan-S-D and toluene. Therefore these values have not been included in table 3.1.

3.3. Assigned Values of log A for Abstraction by Methyl

For reaction of CH_3 with alkanes we have generally assigned a value of log $(A/M^{-1}s^{-1}) = 9.0$ per primary hydrogen (see section 1 and table 1.1). For toluene and propylene, log $(A/M^{-1}s^{-1})$ is assigned as 8.0 on the assumption that resonance interaction would stiffen the reacting molecule with the loss of an additional 4 entropy units compared to a reaction of a primary alkane position. Eachus et al. [6] observed that secondary benzylic positions have a slightly higher A-factor than primary benzylic positions and in turn tertiary benzylic positions have a still higher A-factor (see table 3.3). We have incorporated these observed differences into our estimates. Allylic carbon-hydrogen bonds are assumed to parallel the corresponding aralkane. In the cyclic olefins the value of log A is increased 0.5 over the similar straight chain molecules since the cyclic structure already has limited rotation.

3.4. Absolute Data for Ethyl Radical Reactions

The photolyses of 3-pentanone (diethyl ketone) neat [18] and in perfluorodimethylcyclobutane [19] yield information on the rate of H-atom transfer from 3-pentanone to ethyl radical. The important reactions involving ethyl radical are

$$C_2H_5\cdot + CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3 \rightarrow C_2H_6 + CH_3\dot{C}H\overset{\overset{O}{\|}}{C}CH_2CH_3 \quad (26)$$

$$2C_2H_5\cdot \rightarrow C_4H_{10} \quad (27)$$

$$2C_2H_5\cdot \rightarrow C_2H_6 + C_2H_4 \quad (28)$$

At low concentrations of ketone, reaction (28) is an important source of C_2H_6. Since $k_{28} \ll k_{27}$ [20], the rate of ethane formation may be expressed as

$$d[C_2H_6]/(d[C_4H_{10}])^{1/2} = k_{26}\,[\text{3-pentanone}]/k_{27}^{1/2}. \quad (29)$$

The ratio $k_{26}/k_{27}^{1/2}$ has been evaluated to be 0.0064 $(M^{-1}s^{-1})^{1/2}$ in neat ketone at 301 K and 0.010 $(M^{-1}s^{-1})^{1/2}$ in perfluorodimethylcyclobutane at 299 K. The value of $k_{27}+k_{28}$ in liquid ethane has been evaluated by Fessenden [21] to be

$$\log (k_{27}+k_{28}) = 10.11 - 0.83/\theta,$$

in the temperature range of 96 to 133 K. Assuming this expression to apply, at 301 K, $k_{27}/M^{-1}s^{-1} = 3.2\times 10^9$ (ignoring k_{28}) which is slightly less than observed for $CH_3\cdot$, as expected. Thus at 301 K $k_{26}/M^{-1}s^{-1} = 90$ per α-hydrogen in the ketone solution and 1.4×10^2 in perfluorodimethylcyclobutane. Recent gas phase data extraploated to this temperature give a value of $92\pm 7\times 10^2$ [16]. The agreement between this gas phase value and the value found in ketone solution is remarkable. The analysis of data for k_{26} in ketone solution gives an Arrhenius expression $\log k = 5.2 - 5.18/\theta$ per α-C—H bond. The exceptionally low value of $\log A$ suggests that the system has been oversimplified and that, while values of k are valid within a factor of two over the range investigated, the observed temperature dependence is not a correct measure of the E for k. Assigning a value of $\log A = 8.2$ per α-C—H bond in 3-pentanone solvent for reaction (26) gives

$$\log k = 8.2 - 8.60/\theta.$$

At 350 K, $k/M^{-1}s^{-1} = 680$.

The larger rate constant for C_2H_5 radical found in perfluorodimethylcyclobutane is consistent with results for $CH_3\cdot$ where the same effect was observed. Thus the effect is probably real; however, it is impossible to determine whether it is due to slower radical combination in the perfluorinated solvent or to a true solvent effect on the abstraction reaction.

Kodama et al. [22] have studied the photolysis of azoethane in n-heptane. After correction for ethane from disproportion of ethyl radical within and outside the initially formed cage, they estimated the rate constant for reaction

$$C_2H_5\cdot + \text{n-heptane} \rightarrow C_2H_6 + C_7H_{15}\cdot,$$

relative to $k_{27}^{1/2}$.

$$k_{26}/k_{27}^{1/2} = 1.2\times 10^{-4}\ (M^{-1}s^{-1})^{1/2} \text{ at } 273 \text{ K},$$

the value of k_{27} from reaction (30) at 273 K is 2.8×10^9 therefore

$$k_{26}/M^{-1}s^{-1} = 6.3 \text{ at } 273 \text{ K},$$

$$k_{26}/M^{-1}s^{-1} = 0.63 \text{ per sec C—H bond.}$$

Using a value of $\log (A/M^{-1}s^{-1}) = 9.2$ gives

$$\log (k/M^{-1}s^{-1}) = 9.2 - 11.74/\theta.$$

At 350 K, $k/M^{-1}s^{-1} = 74$.

3.5. Error Limits

The values for $CH_3\cdot$ reactions are derived by a number of steps and undoubtedly involve greater uncertainties than the $C_2H_5\cdot$ data. Because of the uncertainties of the photolysis experiments as well as the extrapolation of the value of k_{27}, the rate constant values calculated for $C_2H_5\cdot$ should be considered certain to only a factor of 2. The rate constants for $C_2H_5\cdot$ calculated above are about a factor of 2 larger than the corresponding data in table 3.1 for $CH_3\cdot$. While the reactions of $C_2H_5\cdot$ and $CH_3\cdot$ with both a secondary alkyl C—H bond and a 3-pentanone α-C—H bond are exothermic, the methyl radical reactions are more exothermic and expected to have a slightly smaller activation energy and therefore be slightly faster. Thus based on the comparison with the $C_2H_5\cdot$ data, the activation energies for CH_3 reaction may be too large by 4 kJ/mol (1 kcal/mol).

TABLE 3.1. Methyl radical-organic compounds: summary of absolute rate parameters

Type of bond	$k/M^{-1}s^{-1}$	Temp. K	log $(AM^{-1}s^{-1})$[g]	E kJ/mol	E (kcal/mol)	Calc k[f] 350 K
Aliphatic (ave)						
Primary[a]	28	383	9.0	55.4	(13.24)	5.4
Secondary[b]	18	343	9.2	52.2	(12.47)	26
Tertiary[a]	1300	383	9.4	46.1	(11.02)	330
Olefinic (ave)						
Primary[a]	260	383	8.0	41.0	(9.79)	77
Secondary[a]	600	383	8.2	39.8	(9.50)	190
Tertiary[a]	1860	383	8.4	37.6	(8.99)	610
Benzylic						
Toluene[a] (pri)	280	383	8.0	40.7	(9.73)	84
Ethylbenzene[a] (sec)	120[c]	323	8.2	37.8	(9.02)	370
	1160[a]	383				
Diphenyl methane[c] (sec)	420	323	8.2	34.5	(8.24)	1100
Cumene[a,c] (tert)	380[c]	323	8.4	35.7	(8.54)	1200
	3650[a]	383				
Phenylcyclohexane[c] (tert)	320	323	8.4	36.5	(8.71)	920
Triphenyl methane[c] (tert)	2000	323	8.4	31.5	(7.54)	4900
Cyclo Aliphatic						
C_5[a]	107	383	9.2	52.6	(12.57)	22
C_6[a]	87	383	9.2	53.3	(12.72)	18
C_7[a]	130	383	9.2	52.0	(12.42)	28
C_8[a]	230	383	9.2	50.2	(11.98)	52
Cyclo Allylic						
C_6[a]	320	383	8.7	45.4	(10.86)	83
Ketones						
Acetone[d] (pri)	10.6	313	8.0	41.8	(9.99)	58
Diethylketone[e] (sec)	160	333	8.2	38.2	(9.14)	310
Diisopropyl ketone[e] (tert)	610	343	8.4	36.9	(8.81)	790
Carboxylic Acids						
Acetic (pri)[e]	22	353	8.0	45.0	(10.75)	19
Propionic (sec)[e]	260	353	8.2	39.1	(9.34)	230
Ethers						
Diethyl (sec)[a]	2200	383	8.5	37.8	(9.04)	720
Diisopropyl (pri)[a]	5700	383	8.7	36.3	(8.66)	2000

[a] Calculated from reactivity relative to a secondary aliphatic position (ref. 7) and the absolute rate data in this table for the secondary aliphatic position (see text).

[b] Calculated from the relative reactivity of acetophenone and the 4-position of n-heptane (ref. 28) and the absolute data for acetone in this table, assuming the α-position of acetone and acetophenone have the same reactivity (see text).

[c] Calculated from the reactivity relative to toluene (ref. 6) and the absolute rate data for toluene in this table (see text).

[d] Calculated from liquid acetone photolysis data (ref. 8, 9, 10, 11, 12) and absolute rate data for the combination of methyl radicals (ref. 13 and 14) (see text).

[e] Calculated from the reactivity relative to 4- position of n-heptane (ref. 28, 29, 20) and the absolute rate parameters for secondary aliphatic position in this table.

[f] Absolute rate constant at 350 K calculated from log A and E.

[g] Assigned; see table 1.1.

TABLE 3.2. Methyl radical-alkanes and cycloalkanes

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Alkane, pri (ave)	t-BuSD	Reactant	383	5.5×10^{-4}	7
Alkane, sec (ave)				24×10^{-4}	7
Alkane, tert (ave)				260×10^{-4}	7
Heptane, pri	Heptane 4-H	Heptane	353	0.1	5
sec				1.0	5
Cyclopentane				1.42	22
Cyclohexane				0.89	22
Methylcyclopentane tert				13.7	22
Methylcyclohexane tert				9.6	22
trans-decalin, tert				6.65	22
Cis-decalin, tert				17.9	22

TABLE 3.3. Methyl radical-aralkanes: benzyl CH

Substrate	Standard	Solvent	Temp K	k/k_s	$\log \frac{A}{A_s}$	$-(E-E_s)$ kJ/mol	$-(E-E_s)$ (kcal/mol)	Reference
Toluene	t-BuSD	Reactant	383	55×10^{-4}				7
o-Xylene	Toluene		323	1.03	-0.10 ± 0.05	1.1 ± 0.2	(0.26 ± 0.04)	6
m-Xylene	Toluene			1.02	-0.10 ± 0.05	0.8 ± 0.3	(0.20 ± 0.06)	6
p-Xylene	t-BuSD		383	61×10^{-4}				7
p-Xylene	Toluene		323	1.16	-0.10 ± 0.05	1.3 ± 0.2	(0.31 ± 0.06)	6
Mesitylene	Toluene			1.02	-0.31 ± 0.15	2.0 ± 0.2	(0.47 ± 0.06)	6
Ethylbenzene	t-BuSD		383	228×10^{-4}				7
Ethylbenzene	Toluene		323	4.63	0.70 ± 0.05	3.0 ± 0.2	(0.71 ± 0.06)	6
Diphenylethane	Toluene			4.34	0.15 ± 0.05	3.1 ± 0.2	(0.73 ± 0.07)	6
Indan	Toluene			9.2	0.20 ± 0.10	5.0 ± 0.5	(1.19 ± 0.12)	6
Tetralin	Toluene			14[a]	-0.22 ± 0.10[a]	9.2 ± 0.6	(2.19 ± 0.15)	6
Cumene	t-BuSD		383	730				7
Cumene	Toluene		323	14.5	0.43 ± 0.05	4.4 ± 0.4	(1.06 ± 0.08)	6
p-t-Butyl Cumene	Toluene			16.9	0.35 ± 0.10	5.3 ± 0.6	(1.27 ± 0.15)	6
Cyclohexylbenzene	Toluene			12.3	0.48 ± 0.10	3.7 ± 0.7	(0.89 ± 0.15)	6
Diphenylmethane				16.2	0.52 ± 0.15	4.1 ± 0.9	(0.98 ± 0.22)	6
Triphenylmethane				77.1	0.9 ± 0.4	6.7 ± 3.3	(1.6 ± 0.6)	6
o-Chlorotoluene			373	0.5				23
p-Chlorotoluene				1.0				23
p-Bromotoluene				0.9				23
p-Phenoxytoluene				0.76				23

[a] Assumes 4 active C-H bonds.

TABLE 3.4. Methyl radical-alkylnaphthalenes: α-CH

Compound and position	Standard	Solvent	Temp. K	k/k_s	Reference
1-Methylnaphthalene	Toluene	Reactants	330	0.8	24
2-Methylnaphthalene				2.05	
1,2-Dimethylnaphthalene				1.06	
2,6-Dimethylnaphthalene				1.08	
1,5-Dimethylnaphthalene				1.09	
1-Ethylnaphthalene				4.26	
2-Ethylnaphthalene				4.27	

TABLE 3.5. Methyl radical-alkenes

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Pri allylic	t-BuSD	Reactants	383	50×10^{-4}	7
Sec allylic	t-BuSD			120×10^{-4}	7
Tert allylic	t-BuSD			370×10^{-4}	7
Propylene	Isooctane	Reactants	338	<0.4	25
2-Methylpropylene				0.37	
Cis-butene-2				0.81	
Trans-butene-2				0.53	
Butene-1				3.3	
Pentene-1				4.1	
Heptene-1				6.3	
Decene-1				6.3	
Hexadecene-1				6.4	
3-Methylbutene-1				22.1	
1,2-Pentadiene				8.8	26
1,4-Pentadiene				20	26
1,5-Hexadiene				4.9	26
1,3-Dimethylenecyclobutane				42.5	26
2,5-Dimethylhexadiene-1,5				4.2	26
2,5-Dimethylhexadiene-2,4				0.5	26

TABLE 3.6. Methyl radical-cycloalkenes: allylic CH

Substrate	Standard	Solvent	Temp. K	k/k_s	Reference
Cyclopentene	Isooctane	Reactants	358	0.81	27
Cyclohexene	t-BuSD		383	62×10^{-4}	7
Cyclohexene	Isooctane		358	0.15	27
Cycloheptene				0.62	
Cyclooctene				0.40	
Cyclopentadiene				30.	
Cyclohexadiene-1,3				51.	
Cycloheptadiene				17.	
Bicycloheptene				< 2.	

TABLE 3.7. Methyl radical-ketones: α-CH

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Diethyl ketone[a]	n-Heptane	Reactants	333	15.3 ± 0.2	28
Di-n-propyl ketone[a]				15.8 ± 0.4	28
Di-n-butyl ketone[a]				13.6	28
Cyclopentanone[a]				19.8 ± 0.4	28
Cyclohexanone[a]				16.2 ± 0.2	28
Di-isopropyl ketone[a]			343	34.0 ± 0.2	28
Acetophenone[a]			343	2.45 ± 0.1	28
Propiophenone			363	25.0 ± 0.4	28
Isobutyrophenone			353	20.0 ± 0.2	28

[a] Data at other temperatures in reference.

TABLE 3.8. Methyl radicals-acids: α-CH

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Acetic acid[a]	n-Heptane	Reactants	353	0.72[b]	29, 30
Propionic acid[a]				8.50[b]	29, 30
Butric acid				8.0[b]	29
Valeric acid				9.0[b]	
Caproic acid				7.5[b]	
Heptanoic acid				8.5[b]	
Isobutyric acid				16.5[b]	
Cyclohexane carboxylic acid				19.5[b]	

[a] Data at various temperatures in references.

[b] Reactivity per α-CH bond assuming no reaction at other positions.

TABLE 3.9. Methyl radical-miscellaneous organic compounds

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Chlorobromo methane	Toluene	Reactants	321.5	0.6	31
Dichlorobromomethane	Toluene		338	30	
Methyl β,β-dimethylacrylate β-CH	Isooctane			1.3	32
β,β-dimethylacrylonitrile				2.1	
1-Cyclopentenecarbonitrile				12.3	
Methylphenyl ether	t-BuSD		383	99×10^{-4}	7
Ethylphenyl ether α-CH				160×10^{-4}	
Dioxane				120×10^{-4}	
Diethyl ether α-CH				440×10^{-4}	
Diisopropyl ether α-CH				1100×10^{-4}	

References for Section 3

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4. Reactions of Trichloromethyl Radical

The ease of generating the trichloromethyl radical under controlled conditions has encouraged the study of this radical, and a good balance of absolute and relative rate data has been obtained. Except for the early studies on this radical, the liquid phase data now appear to be self-consistent. The trichloromethyl radical reactions are of special importance since there now appears to be a distinct difference between gas and liquid phase data as will be discussed below.

4.1. Absolute Rate Measurements

The trichloromethyl radical can be generated by photolysis or radiolysis of CCl_3Br and CCl_4

$$CCl_3{-}X \rightarrow CCl_3\cdot + X\cdot \ (X = Br, Cl), \tag{1}$$

or by H-atom transfer by a carbon radical ($R\cdot$) with CCl_3H, CCl_3Br, or CCl_4

$$R\cdot + CCl_3{-}Y \rightarrow RY + CCl_3\cdot \ (Y = H, Br, Cl). \tag{2}$$

Carbon radicals are generally formed by thermolysis of an azo or peroxide compound or by photolysis of CCl_3X.

$$RN_2R \rightarrow 2R\cdot + N_2 \tag{3}$$

In the presence of H-donor (RH) the following propagation and termination sequence occurs

$$CCl_3\cdot + RH \longrightarrow R\cdot + CHCl_3, \tag{4}$$

$$R\cdot + BrCCl_3 \text{ (or } CCl_4) \longrightarrow RBr \text{ (or } RCl) + CCl_3\cdot, \tag{5}$$

$$2\,CCl_3\cdot \longrightarrow C_2Cl_6, \tag{6}$$

$$CCl_3\cdot + R\cdot \longrightarrow RCCl_3, \tag{7}$$

$$2R\cdot \longrightarrow R{-}R \tag{8}$$

When chain lengths are long, the overall rate of $CHCl_3$ formation of $CHCl_3(R_{CHCl_3})$ or halide formation (R_{RX}) may be expressed

$$R_{CHCl_3} = R_{RX} = \frac{R_i^{1/2} k_4 [RH]}{(2k_6 + (2k_7k_4/k_5)[RH]/[CXCl_3] + (2k_8k_4^2/k_5^2)[RH]^2/[CXCl_3]^2)^{1/2}}, \tag{9}$$

where R_i equals the rate of radical formation. Eq (9) is a variation of eq (7) (section 1) and simplifies at high $[CXCl_3]$ where the expression becomes zero order in $[CXCl_3]$ and only reaction (6) is important for termination:

$$R_{CHCl_3} = R_{RX} = \left(\frac{R_i}{2k_6}\right)^{1/2} k_4[RH]. \quad (10)$$

Alternatively, if R_i, k_7, and k_8 make unknown contributions to the overall rate, then the rate may be expressed as a form of eq (8), section 1

$$R_{RX} = R_{CHCl_3} = k_4[RH]R_{C_2Cl_6}^{1/2}/(2k_6)^{1/2}. \quad (11)$$

Thus the ratio of $k_4/k_6^{1/2}$ can be determined in two different ways. From this ratio the value of k_4 may be readily determined since k_6 has been estimated. The best value of $k_6/M^{-1}s^{-1}$ is 5.0 ($\pm$2.5) $\times 10^7$ and is independent of temperature. This value is an average of values obtained by following the decay of trichloromethyl radical by esr [1], by the rotating sector technique where the change in liquid volume is used as a measure of reaction [2 and 3] and by a decay technique where liquid volume and heat accumulation are monitored to follow the reaction [4]. The good agreement among the variety of methods seems to offer strong support for the average value cited here. However, this average value is in strong disagreement with the gas phase values reported for this combination reaction of 3.9 x 10^9, 4.6 x 10^9, and 7.9 x 10^9 [5, 6, 7]. There is some evidence that the rotating sector technique over-estimates the rate constant for gas phase combination of simple alkyl radicals [8] and possibly this is also true for the trichloromethyl radical. Alternatively, there may be a true solvent effect on the reaction as a result of the polar trichloromethyl radical [1].

The rotating sector and photochemical after-effect techniques give absolute values of k_4 as well as k_6. Since these techniques have relied generally on volume contraction for determining the conversion, the reactions studied have largely involved addition of $CCl_3\cdot$ to a double bond rather than abstraction of hydrogen as in reaction (4)

$$CCl_3\cdot + C{=}C \rightarrow CCl_3{-}C{-}C\cdot, \quad (12)$$

followed by

$$CCl_3{-}C{-}C\cdot + CCl_3X \rightarrow CCl_3{-}C{-}CX + CCl_3\cdot \quad (13)$$

For most olefins with an allylic C—H, k_4 and k_{12} complete and the ratio of k_4/k_{12} has been determined in several cases [9]. Therefore the value of k_4 can be determined from values for k_{13} and k_4/k_{13}.

4.2. Relative Rate Measurements

Most of liquid-phase structure-reactivity data we have for trichloromethyl radical comes from competitive reactions where the value of k_4 has been measured for several substrates relative to k_4 for a reference compound [10]. For example in the competitive bromination of two hydrocarbons, R_1H and R_2H, the following kinetic expression applies

$$\frac{\Delta[R_1H]}{\Delta[R_2H]} = \frac{[R_1Br]}{[R_2Br]} = \frac{k_4}{k_4'} \times \frac{[R_1H]}{[R_2H]}. \quad (14)$$

At low conversions it is necessary to use product formation to determine relative reactivity (k_4/k_4'), the precision of k_4/k_4' being approximately the sum of the precision of the two measured products. However, for less stable products, analysis by gas chromatography may not be feasible. Thus it is necessary to measure the decrease in hydrocarbon, and high conversions are needed. The precision of k_4/k_4' measured in this way is less than that obtained by measuring the products because the precision of ΔR_1H and ΔR_2H is not as large, but generally the precision increases linearly with conversion. At high conversions, eq (14) is no longer valid and the integrated form must be used [10].

4.3. Absolute Rate Parameters

Most of the kinetic data for the $CCl_3\cdot$ abstraction have been measured at one temperature or over an insufficient temperature span to define E or A adequately. Therefore we have assumed values of A to be consistent with the values of A chosen for other H-atom transfers covered in this review (see table 1.1, section 1) and have calculated E from experimental values of k and $\log A$.

4.4. Error Analysis

If the value for the combination of trichloromethyl radicals in the liquid phase is within the indicated limit of 5.0 ($\pm$2.5) 10^7 $M^{-1}s^{-1}$, the value of k_4 obtained directly from the ratio $k_4/k_6^{1/2}$ (known to $\pm$20%) is valid to about $\pm$40%. While there is some uncertainty in the $\log A$ values as well as the E values these errors tend to compensate. For example, the Arrhenius values give the measured value of k_4 at mean experimental temperature, but at 50 K above or below the mean temperature the added uncertainty due to the uncertainties in E_a and A are $\pm$20%. Thus the calculated values of k_4 in table 4.1 should be accurate within $\pm$60%.

4.5. Tables

Tables 4.1 through 4.6 summarize absolute and relative rate data for trichloromethyl radical. Table 4.1 summarizes absolute rate constants and rate parameters for H-atom transfer by trichloromethyl radical from a representative series of organic compounds.

Some values for k were measured directly and others were calculated from relative values listed in tables 4.2–4.6. In principle, all relative values of k may be converted to absolute values using known absolute values for key reference compounds. Units for absolute rate constants are in $M^{-1}s^{-1}$ units; relative rate data are unitless.

TABLE 4.1. Trichloromethyl radical-organic compounds: summary of absolute rate constants and rate parameters

Substrate and position	$k/M^{-1}s^{-1}$ per CH	Temp. K	Log A [a]	E [b] kJ/mol (Kcal/mol)	Calc k [d] 300 K	Calc k [d] 400 K	Reference
Cyclohexane	0.013	298	9.2	3.25 (15.11)	0.015	8.7	11
Cyclohexene 3-CH	84	298	8.7	38.68 (9.24)	93	4500	2, 4, 9
1-Heptene 3-CH	170	313	8.2	35.79 (8.55)	94	3400	4, 9
Toluene	1.1	328					12
α-CH	2.2	340.5					12
	4	353					12
	9.3	373	8.0	49.96 (11.93)	0.20	30	12
Ethylbenzene α-CH	24 [c]	313	8.2	40.95 (9.78)	12	720	Table 2
Cumene α-CH	122 [c]	313	8.4	37.86 (9.04)	65	2900	Table 2
sec-Butylbenzene α-CH	210 [c]	343	8.4	39.94 (9.54)	28	1500	Table 2
3-Butylbenzene	74 [c]	343	8.4	42.91	8.6	630	Table 2
Diphenylmethane	24 [c]	313	8.2	40.95 (9.78)	12	720	Table 2
Triphenylmethane	75 [c]	313	8.4	39.12	40	2000	Table 2
Isopropanol 2-CH	3.0	298	8.7	11.21 48.65 (46.91) (11.62)	3.4	378	13
Benzaldehyde 1-CH	335 [c]	353	8.7	41.73 (9.97)	27	1780	Table 4
α-Methyoxytoluene α-CH	214 [c]	353	8.2	39.69 (9.48)	20	1000	Table 3

[a] Assigned.
[b] Calculated from assigned value of A and experimental value of k.
[c] Evaluated from relative reactivity in tables 2, 3, or 4 and calculated rate constant for the standard compound using parameters in this table.
[d] Calculated from $\log k = \log A - E/\theta$.

TABLE 4.2. Trichloromethyl radical-aralkanes: relative reactivities of benzyl CH

Substrate	Standard	Solvent	Temp. K	k/k_s	Reference
Toluene [a]	Toluene	Reactants	313	1.0	
Ethylbenzene	Toluene	Reactants	313	50 ± 5	10
Ethylbenzene	Cumene	Benzene	343	0.154 ± 0.005	15
o-Diethylbenzene	Fluorene	CCl_3Br	343	0.86 ± 0.06	16
Propylbenzene	Cumene	Benzene	343	0.122 ± 0.01	15
Cumene [b]	Toluene	Reactants	313	2.60 ± 0.01	10
iso-Butylbenzene	Cumene	Benzene	343	0.042 ± 0.002	15
sec-Butylbenzene	Cumene	Benzene	343	0.48	15
Neopentylbenzene [c]	Cumene	Benzene	343	0.006	15
3-Pentylbenzene	Cumene	Benzene	343	0.169	15
Diphenylmethane	Toluene	Reactants	313	50 ± 5	10
Triphenylmethane	Toluene	Reactants	313	160 ± 16	10
1,1-Diphenylethane	Toluene	Reactants	313	650 ± 65	10
Benzocyclobutene	Fluorene	CCl_3Br	343	0.076 ± .004	16
Benzocyclopentene (Indan)			343	1.39 ± .08	16
Benzocyclohexene (Tetralin)			343	1.14 ± .08	16
Benzocycloheptene			343	0.84 ± .06	16
1-Methylnaphthalene [d]	Toluene	Benzene	343	5.8 ± 0.3	19
2-Methylnaphthalene		Benzene	343	4.0 ± 0.6	19
1-Methylanthracene		Benzene	343	76. ± 6	19
9-Methylanthracene		Benzene	343	650 ± 60	

[a] Effect of ring substitution on reactivity at 323 K in reference 14.
[b] Investigation of effect of p- and m-substitution on cumene reactivity at 343 K in reference 17.
[c] Effect of p- and m- substitution on reactivity at 343 K in reference 18.
[d] See reference 19 for other methyl substituted polyaromatics.

TABLE 4.3. Trichloromethyl radical-ethers: relative reactivities

Substrate and position [a]	Standard	Solvent	Temp. K	k/k_s	Reference
α-Methoxy toluene [b]	Toluene	CCl_4	353	52 ± 5	20
α-Methoxy diphenylmethane				108 ± 5	20
α,α-Dimethoxy toluene				50 ± 3	20
Dibenzyl ether				34 ± 4	20

[a] CH adjacent to oxygen.
[b] Data for ring substituted compounds in reference 20.

TABLE 4.4. Trichloromethyl radical-aldehydes: relative reactivities

Substrate	Standard	Solvent	Temp. K	k/k_s	Reference
Benzaldehyde [a]	Ethylbenzene	CCl_4	353	2.40 ± 0.02	22
p-t-Butylbenzaldehyde				3.46 ± 0.16	22
p-Chlorobenzaldehyde				1.56 ± 0.02	22

[a] Additional data on ring substituted compounds are included in references 21, 22 and 23.

TABLE 4.5. Trichloromethyl radical-cycloalkanes: relative reactivity

Substrate and position	Standard	Solvent	Temp. K	k/k_s	Reference
Bicyclo [2.2.1]-heptane	Adamantane [a] 1-CH	Reactants	313		
1-CH				0.00	24
2-CH				0.67 ± 0.07	24
Bicyclo [2.2.2]-octane					
1-CH				1.11 ± 0.15	24
2-CH				1.92 ± 0.23	24
Bicyclo [3.3.1]-nonane					
1-CH				16.0 ± 0.8	24
Adamantane [a]					
2-CH				0.5 ± 0.1	24
1,1-Diadamantane				1.47 ± 0.08	25
1-Methyladamantane				1.29 ± 0.06	25
1-Methoxyadamantane				0.75 ± 0.04	25
1-Carbomethoxyadamantane				0.62 ± 0.03	25
1-Bromoadamantane				0.37 ± 0.02	25
1-Cyanoadamantane				0.37 ± 0.03	25
Homoadamantane [b]					
3-CH				40.3 ± 2.0	24

[a] Adamantane is tricyclo [1.1.1.1] decane.
[b] Homoadamantane is tricyclo [$2.1.1^{1,5}.1^{3,8}$] undecane.

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5. Alkoxy Radicals

The reaction of molecular oxygen with organic compounds in the liquid phase proceeds by way of one or more radical chain sequences involving peroxy (RO_2) and often alkoxy (RO) radicals.

Although the detailed reactions of alkoxy radicals are often quite complex, relative rates of H-atom transfer from two or more substrates can be obtained relatively easily and, through a common standard, related to an absolute value. As a result, we have available many absolute rate constants for H-atom transfer by t-butoxy radicals from a variety of organic compounds.

5.1. Relative and Absolute Rate Measurements

Almost all the extensive data for alkoxy radical abstractions refer to t-butoxy radical (t-BuO) because of the ease with which this radical may be generated from the corresponding peroxide, oxalate, hyponitrite, and particularly from the hypochlorite.

Relative reactivities of organic compounds toward t-BuO (k/k') may be measured in competitive experiments where two substrates (R_1H and R_2H) react with t-BuO and the product radicals then form products such as organic chlorides by reactions with CCl_4 solvent.

$$\text{t-BuO}\cdot \xrightarrow{k_d} \text{acetone} + \text{Me}\cdot$$
$$\text{t-BuO}\cdot \xrightarrow[R_1H]{k} \text{t-BuOH} + R\cdot_1 \xrightarrow{CCl_4} R_1Cl$$
$$\text{t-BuO}\cdot \xrightarrow[R_2H]{k'} \text{t-BuOH} + R\cdot_2 \xrightarrow{CCl_4} R_2Cl$$

The ratio of rate constants k/k' may be determined indirectly by comparing ROH/ketone ratios on reaction with each substrate, separately or directly, by determining the relative yields of R_1Cl and R_2Cl or the consumption of reactants in competitive experiments.

Both competitive methods give fairly reliable relative rate constants in most cases. However, discrepancies between them have been found when t-butyl hypochlorite was used as the source of alkoxy radicals and when aralkanes (e.g., toluene) were the substrates. This occurs because of the incursion of a chlorine atom chain and relative reactivities to Cl rather than to t-BuO were determined. Since most of the absolute rate constants reported in this review have been calculated from relative reactivity data obtained from hypochlorite chlorinations, we have been careful not to include data that may be suspect.

To date there have been two stationary state kinetic studies of t-butyl hypochlorite chlorinations [1 and 2] and one nonstationary state study [3]. This reaction can be represented by the following reaction scheme.

Initiation:

$$\text{t-BuOCl} \longrightarrow \text{t-BuO}\cdot + \text{Cl}\cdot \qquad (1)$$

Propagation:

$$\text{t-BuO}\cdot + \text{RH} \xrightarrow{k} \text{t-BuOH} + \text{R}\cdot \qquad (2)$$

$$\text{R}\cdot + \text{t-BuOCl} \xrightarrow{\text{fast}} \text{RCl} + \text{t-BuO}\cdot \qquad (3)$$

Termination:

$$\text{t-BuO}\cdot + \text{t-BuO}\cdot \xrightarrow{k_t} \qquad (4)$$
$$\text{t-BuO}\cdot + \text{R}\cdot \xrightarrow{k_{t'}} \text{Molecular products} \qquad (5)$$
$$\text{R}\cdot + \text{R}\cdot \xrightarrow{k_{t''}} \qquad (6)$$

Carlsson and Ingold [3] found that overall rates (R) of photochemical and α,α'-azobisisobutyronitrile (AIBN) initiated t-butyl hypochlorite halogenation of certain hydrocarbons in CCl_4 at 297 K obeyed the kinetic expression

$$R = \frac{k[RH]R_i^{1/2}}{(2k_t)^{1/2}}. \qquad (7)$$

This suggested that reactions (2) and (4) were the rate

controlling propagation and termination steps. The rotating sector method was used to determine $2k_t(\sim 2\times 10^8$ $M^{-1}s^{-1})$, and values of k were calculated from $k/(2k_t)^{1/2}$. The values of k reported by Carlsson and Ingold were based on an overall heat of reaction of -51 kcal mol^{-1} for the process

$$\text{t-BuOCl} + C_6H_5CH_3 \rightarrow \text{t-BuOH} + C_6H_5CH_2Cl.$$

The overall heat of reaction of the analogous process with cyclohexane has now been accurately determined as -42.4 kcal mol^{-1} by Walling and Papaioannou [4]. If we make the reasonable assumption that ΔH for toluene and cyclohexane are equal Carlsson and Ingold's values of k (per active hydrogen) for toluene fit the equation $\log (k/M^{-1}s^{-1}) = 7.4 - 5.6/2.303RT$. Values of k calculated from this equation at 313 K and 323 K are approximately ten times smaller than the values of this rate constant that have been estimated by Walling and Kurkov [1] and Lorand and Wallace [5]. This discrepancy must be partly because the value of $2k_t$ for t-BuO obtained by Carlsson and Ingold is too low. We have, therefore, converted the relative reactivity data for t-BuO to absolute values using values of k that are *ten times larger* than the values that can be calculated from the above Arrhenius equation. For example, at 313 K, we have used a value of k (per active hydrogen) of 3×10^4 $M^{-1}s^{-1}$.

Activation parameters for reactions of t-BuO are not directly available from experiments except in those few instances where the variation in (k/k_d) with temperature was measured for hydrocarbons [6]. However, in the absence of reliable values for cleavage reaction k_d (those reported seem to be unreasonably low), no reliable values of k can be obtained by this method. Accordingly, we have assigned rates of $\log A$ as shown in table 1.1 and with values of k, calculated E with sufficient precision to recalculate the experimental value of k.

5.2. Errors

We believe that assigned values of $\log A$ have probable errors of ± 0.5 equivalent to ± 0.7 kcal/mol in E at 313 K and represent a factor of 3 in rate constant, well beyond the probable experimental error for these kinds of measurements. Although this error analysis suggests that more accurate activation parameters may be obtained by direct measurements at two temperatures, this may not be the case if experiments are done at temperatures much above 313 K where cleavage of RO and cross termination of alkyl radicals become important.

TABLE 5.1. t-Butoxy radical-organic compounds: summary of absolute rate constants and parameters at 313 K per active hydrogen

RH Bond	$k/M^{-1}s^{-1} \times 10^{-4}$	log $(A/M^{-1}s^{-1})$ [a] (±0.5)	E [b] kJ/mol	(kcal/mol)
Alkane				
pri	0.28	9.0	33.3	(7.95)
sec	3.6	9.2	27.8	(6.65)
tert	12.6	9.4	25.8	(6.16)
cyclic-sec	4.3	9.2	27.4	(6.54)
Alkene				
pri	5.3	8.0	19.6	(4.69)
sec	24	8.2	16.9	(4.04)
tert	52	8.4	16.1	(3.84)
cyclic-sec	111	8.7	15.9	(3.80)
Phenylalkyl				
pri	3.0	8.0	21.1	(5.04)
sec	10.5	8.2	19.0	(4.55)
tert	20.5	8.4	18.5	(4.42)
cyclic-sec	65	8.7	17.3	(4.13)
	15	8.7	21.1	(4.80)
Diphenylmethane	14.1	8.5	20.1	(4.80)
Triphenylmethane	29	8.5	18.2	(4.35)
Ethers (α CH) [c]				
pri	10	8.7	22.2	(5.30)
sec	31	8.7	19.2	(4.59)
cyclic sec 3-ring [d]	27.5	9.0	21.3	(5.10)
cyclic sec 4-ring	58.5	8.7	17.6	(4.20)
cyclic sec 5-ring	42.5	8.7	18.4	(4.40)
cyclic sec 6-ring	22.3	8.7	20.1	(4.80)
Alkyl-X (α CH)				
chloro	1.4	9.0	29.1	(6.95)
cyano	0.18	9.0	34.4	(8.22)
acetoxy	0.81	9.0	30.5	(7.29)
Ketone (α CH)				
pri	0.074 [e]	8.7	34.9	(8.35)
sec	0.6 [e]	8.5	28.3	(6.76)
cyclo	1.0 [e]	8.7	28.2	(6.73)

[a] Assigned: see table 1.1.
[b] Calculated from k and log A.
[c] Extrapolated from 273 K (see table 5.5).
[d] Ring size.
[e] At 273 K.

TABLE 5.3. t-Butoxy radical-alkenes: relative and absolute rate constants and parameters for abstraction at allylic CH bonds at 313 K per reactive hydrogen [7]

Substrate and position	k/k_s [a]	$k/M^{-1}s^{-1} \times 10^{-4}$	log $(A/M^{-1}s^{-1})$ [b]	E [c] kJ/mol	(kcal/mol)
Isobutylene pri-CH	1.19	3.6	8.0	20.6	(4.93)
trans-But-2-ene pri-CH	1.97	5.9	8.0	19.3	(4.62)
cis-But-2-ene pri-CH	2.1	6.3	8.0	19.2	(4.58)
But-1-ene sec-CH	6.0	18	8.2	17.7	(4.22)
cis-Pent-2-ene sec-CH	9.1	27	8.2	16.6	(3.96)
trans-Pent-2-ene sec-CH	9.3	28	8.2	16.5	(3.94)
3-Methylbut-1-ene tert-CH	17.4	52	8.4	16.1	(3.84)
Cyclohexene sec-CH	36.4	109	8.7	15.9	(3.81)
Cyclopentene sec-CH	37.9	114	8.7	15.8	(3.78)

[a] Relative to toluene for which k is 3×10^4 $M^{-1}s^{-1}$ at 313 K.
[b] Assigned; see table 1.1.
[c] Calculated from k and log A.

TABLE 5.2. t-Butoxy radical-alkanes: relative and absolute rate constants and parameters at 313 K per active hydrogen [7]

Substrate and position	k/k_s [a]	$k/M^{-1}s^{-1}\times10^{-4}$	$(A/M^{-1}s^{-1})$ [d]	E [e] kJ/mol	(kcal/mol)
n-Butane					
pri-H	0.1	0.3	9.0	33.1	(7.90)
sec-H	1.2	3.6	9.2	27.8	(6.65)
2,3-Dimethylbutane					
pri-H	0.09 (0.095) [b]	0.27 (0.28) [b]	9.0	33.3	(7.97)
tert-H	4.2 (3.9) [b]	12.6 (11.7)	9.4	25.6	(6.16)
Cyclobutane	0.7	2.1	9.2	29.2	(6.98)
Cyclopentane	1.38	4.14	9.2	27.4	(6.56)
Cyclohexane	1.06–1.59 [c] (1.55) [b]	3.8–4.8 (4.65)	9.2	27–27.7	(6.45–6.61)

[a] Relative to toluene; t-BuO· from photolysis of C_4H_9OBr [8].
[b] C_4H_9O· from photolysis of C_4H_9OBr [8].
[c] The limits of relative reactivities determined using C_4H_9OCl, C_4H_9OBr, di-t-butyl peroxylate and di-t-butyl hyponitrite as sources of t-BuO· [9].
[d] Assigned; see table 1.1.
[e] Calculated from k and log A.

TABLE 5.4. t-Butoxy radical-aralkanes and aralkenes: relative and absolute rate constants and parameters for abstraction at benzyl and/or allylic CH bonds at 313 K per reactive hydrogen

Substrate	k/k_s	$k/M^{-1}s^{-1} \times 10^{-4}$	log $(A/M^{-1}s^{-1})$ [a]	E_p [b] kJ/mol (kcal/mol)		Reference
Toluene [c] (Standard)	1.0	3.0	8.0	21.1	(5.04)	10
Ethylbenzene	4.0	12.0 (11) [d]	8.2	18.6	(4.45)	11
n-Propylbenzene	2.93	9.0	8.2	19.5	(4.65)	10
Cumene	6.84	20.5 (25)	8.4	18.5	(4.42)	10
t-Butylbenzene	0.17	0.5	9.0	31.8	(7.59)	11
Diphenylmethane	4.70	14.1	8.5	20.1	(4.80)	10
Mesitylene	1.34	4.0	8.0	20.3	(4.86)	10
Tetralin	21.6	65	8.7	17.3	(4.13)	11
Fluorene	5.04	15	8.7	21.1	(5.04)	10
Triphenylmethane	9.60	29	8.5	18.2	(4.35)	10
Allylbenzene	3.87	12	7.5	14.5	(3.47)	11

[a] Assigned; see table 1.1.

[b] Calculated from k and log A.

[c] Absolute reactivities (per benzyl hydrogen) of meta and para substituted toluenes can be correlated by the equation $\log (k/M^{-1}s^{-1}) = -(.32-.39)\sigma^{+} + 4.78$.

[d] $C_4H_9O\cdot$ radicals from $C_4H_9OBr\cdot$ [8].

TABLE 5.5. t-Butoxy radical-ethers: relative [a] and absolute rate constants and parameters for abstraction of an α-CH at 273 K per reactive hydrogen [12]

Ether	k/k_s [b] (rel)	$k/M^{-1}s^{-1} \times 10^{-4}$	log $(A/M^{-1}s^{-1})$ [c]	E [d] kJ/mol (kcal/mol)	
Toluene (standard)	1.0	0.87	8.0	21.2	(5.07)
Diethyl ether	12.2	10.6	8.7	19.2	(4.59)
Diisopropyl ether	15.9	13.8	8.7	18.6	(4.45)
Methyl t-butyl ether	3.22	2.8	8.7	22.2	(5.31)
Di-t-butyl ether	0.05	0.045	9.0	33.2	(7.93)
Anisole (methylphenyl ether)	1.0	0.87	8.7	24.9	(5.95)
Phenetole (ethylphenyl ether)	6.5	5.7	8.7	20.6	(4.93)
Ethylene oxide	9.8	8.5	9.0	21.3	(5.08)
Propylene oxide [e]	50.4	44	9.0	17.5	(4.19)
Isobutylene oxide [f]	0.076	0.067	9.0	32.3	(7.71)
Styrene oxide [g]	0.235	0.2	8.5	27.2	(6.49)
Trimethylene oxide	25	22	8.7	17.5	(4.19)
Tetrahydrofuran	17.3	15	8.7	18.4	(4.40)
2,5-Dimethyltetrahydrofuran	75.8	66	8.7	15.1	(3.60)
Tetrahydropyran	8.1	7.0	8.7	20.2	(4.82)
Methylal (dimethoxymethane)	9.3	8.1	8.7	19.8	(4.74)
Dioxane	5.0	4.3	8.7	21.3	(5.08)

[a] Relative to toluene for which k at 273 K is $0.87 \times 10^4 M^{-1}s^{-1}$.

[b] Average error in k (rel) given as 8 percent.

[c] Log A assigned; see table 1.1.

[d] Calculated from k and log A.

[e] Assume two reactive hydrogens.

[f] Assumes eight reactive hydrogens.

[g] Assumes three reactive hydrogens.

TABLE 5.6. t-Butoxy radical-organic compounds: relative [a] and absolute rate constants and parameters at 313 K per reactive hydrogen [13]

Substrate and position	k/k_s [a]	$k/M^{-1}s^{-1} \times 10^{-4}$	log $(A/M^{-1}s^{-1})$ [b]	E [c] kJ/mol (kcal/mol)	
1-Chlorobutane					
1-CH	0.46	1.4	9.0	29.1	(6.95)
2-CH	0.41	1.2	9.2	30.7	(7.33)
3-CH	0.92	2.8	9.2	28.5	(6.80)
4-CH	0.22	0.66	9.0	31.0	(7.42)
Butyronitrile					
1-CH	0.060	0.18	9.2	35.6	(8.51)
2-CH	0.12	0.36	9.2	33.8	(8.08)
3-CH	0.060	0.18	9.0	34.4	(8.22)
n-Propyl acetate					
1-CH	0.27	0.81	9.0	30.5	(7.29)
2-CH	0.40	1.2	9.2	30.7	(7.33)
3-CH	0.15	0.45	9.2	41.0	(7.94)
Acetoxy CH	0.047	0.14	9.0	33.2	(8.38)

[a] Relative to toluene for which k is $3 \times 10^4 M^{-1}s^{-1}$ at 313 K.
[b] Assigned; see table 1.1.
[c] Calculated from k and log A.

TABLE 5.7. t-Butoxy radical-organic compounds: relative [a] and absolute rate constants and parameters for H-atom transfer at 273 K adjacent to a functional group per reactive hydrogen [11]

Substrate	k/k_s [a]	$k/M^{-1}s^{-1} \times 10^{-4}$	log $(A/M^{-1}s^{-1})$ [c]	E [d] kJ/mol (kcal/mol)	
Methyl formate	6.42	5.6	8.7	20.7	(4.94)
Methylene chloride	0.35	0.3	8.7	27.3	(6.52)
Chloroform	3.24	2.8	8.7	22.1	(5.31)
Acetone	0.085	0.074	8.5	30.5	(7.28)
t-Butyl alcohol	0.043	0.037	9.0	32.0	(7.65)
3-Pentanone	0.69	0.6	8.5	25.5	(6.10)
Cyclopentanone [b]	0.14	1.0	8.5	23.5	(5.62)
Acetophenone	0.107	0.09	8.5	29.0	(6.93)
Methyl benzoate	0.040	0.035	8.7	32.1	(7.69)
Phenyl acetate	0.029	0.025	8.7	32.9	(7.87)

[a] Relative to toluene for which k at 273 K is $0.87 \times 10^4 M^{-1}s^{-1}$.
[b] At 313 K.
[c] Assigned; see table 1.1.
[d] Calculated from k and log A.

References for Section 5

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6. Peroxy Radicals

The great technical importance of autoxidation has stimulated much of the research to elucidate mechanisms and kinetics, to predict products and rates, and ultimately to measure absolute rate constants for all important elementary rate steps in oxidation [1, 2 and 3]. As a result, we have available many more reliable absolute rate constants for $RO_2\cdot$ (in the liquid phase) than for any other radical [4].

6.1. Relative Rate Constants

Oxidations of mixtures of organic compounds or of two or more different CH bonds in a single molecule is the most common procedure for evaluating relative reactivities [5, 6 and 7]. Under most conditions the values for k(rel) are independent of values for k_t; however, as measured in cooxidation, k(rel) is usually a composite of two rate constants for H-atom transfer by one alkylperoxy radical toward both substrate CH bonds. Although capable of giving valuable information concerning reactivity of different organic compounds toward $RO_2\cdot$ radicals, cooxidations require exceptional care in analyses to avoid very large errors [6] and have been all but superseded by the technique of added hydroperoxide [8] discussed below. Relative reactivity data may be used to estimate absolute rate constants only if relative data refer to a single type of $RO_2\cdot$ radical such as tertiary or secondary, as the absolute reactivities of peroxy radicals vary in the order tert:sec:prim = 1:5:10 [9]. Because of the large number of absolute constants available, no relative data are included in this review.

6.2. Absolute Rate Constants

The same kinetic considerations discussed in connection with determination of k for $RO\cdot$ apply equally to reactions of RO_2 and eq (4) in section 5 above may be used directly with rotating sector or esr methods to evaluate $2k_t$ and k.

Typically, rates of oxidation are followed by changes in oxygen pressure with time. For this reason, and unlike with most chain reactions, reliable measurements of changes in reactant concentration may be made at very low conversions (~1%) of hydrocarbon. This is a fortunate circumstance for in most autoxidations the primary product is either a hydroperoxide (ROOH) or a polyperoxide $[CH_2CH_2{-}OO]_n$, neither of which is stable thermally or in the presence of transition metal ions.

Accurate and precise measurements of absolute or composite rate constants $(k/(2k_t)^{1/2})$ in autoxidations are obtainable only if the following experimental precautions are taken:

(1) Rate of initiation is known through the use of an added initiator.
(2) Oxygen pressure is high enough (> 100 mm) and stirring or shaking fast enough to ensure an adequate rate of oxygen diffusion.
(3) Temperature is low enough (< 373 K) to minimize formation and cleavage of alkoxy radicals.
(4) System is free ($< 10^{-6}M$) of transition metal ions that decompose peroxides and free of inhibitors.
(5) Conversion is low enough (2–5%) to avoid decomposition of hydroperoxides and oxidation of primary products.
(6) Product analyses can account for > 75% of the absorbed oxygen.

Observation of the foregoing requirements will usually permit one to measure composite rate constants to about ±20% accuracy and absolute rate constants to ±50%, if the substrate has only one reactive site (> 90% reaction) or equivalent sites. Error limits may be much higher if several different CH bonds are involved in competitive oxidation or if several different radicals participate in termination steps.

The literature records many efforts to measure autoxidation rate parameters for composite rate constants, and from this information coupled with assumptions concerning values of E_t, to estimate values of E. Most estimates are probably in significant error owing to failure of the system to meet all the foregoing requirements, particularly (3) and (5) as shown by the wide variation in E reported by different investigators [2].

For all these reasons, autoxidation in the presence of added hydroperoxide is a powerful and alternative technique for simplifying oxidation kinetics and providing an accurate value of k with one measurement [8]. By proper choice of substrate and added hydroperoxide, it becomes possible to evaluate many combinations of $RO_2\cdot$ and RH. The principle of this procedure rests on the rapid chain transfer between $RO_2\cdot$ and added R'OOH ($k \sim 10^3 M^{-1}s^{-1}$). In a typical chain sequence:

Initiation: $\mathrm{In} \xrightarrow{k_d} 2\mathrm{X}\cdot$ (1)

$\mathrm{X}\cdot + \mathrm{RH} \longrightarrow \mathrm{XH} + \mathrm{R}\cdot$ (2)

$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{\text{fast}} \mathrm{RO_2}\cdot$ (3)

Propagation: $\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k} \mathrm{ROOH} + \mathrm{R}\cdot$ (4)

$\mathrm{RO_2}\cdot + \mathrm{R'OOH} \longrightarrow \mathrm{RO_2H} + \mathrm{R'O_2}\cdot$ (5)

$\mathrm{R'O_2}\cdot + \mathrm{RH} \xrightarrow{k'} \mathrm{R'O_2H} + \mathrm{R}\cdot$ (6)

Termination: $2\mathrm{R'O_2}\cdot \xrightarrow{k_t'} \text{Termination}$ (7)

$2\mathrm{RO_2}\cdot \xrightarrow{k_t} \text{Termination}$ (8)

$\mathrm{RO_2}\cdot + \mathrm{R'O_2}\cdot \xrightarrow{k_t''} \text{Termination}$ (9)

If enough hydroperoxide is added to ensure that all $RO_2\cdot$ are converted to $R'O_2\cdot$, the kinetic expression for oxidation becomes (with long chains)

$$\mathrm{R} = (\mathrm{R_i}/2k_t')^{1/2}k'[\mathrm{RH}],$$

where $R_i = 2ek_d[In]$.

The several advantages of this procedure over autoxidation are:

(1) The reactivity of a series of substrates to one peroxy radical can be determined, free from differences in the reactivity of the peroxy radical.
(2) Since the termination rate constant (k_t') does not change, the ratio $k'/(2k_t')^{1/2}$ gives much more reliable *relative* reactivities than does $k/(2k_t)^{1/2}$.
(3) Addition of a hydroperoxide, which gives a peroxy radical with a low value of k_t' (e.g., t-butyl hydroperoxide), can significantly increase the chain length of an autoxidation. Thus reliable values of k' can be determined for substrates that normally oxidize too slowly to give reliable values of k by a nonstationary state method.

As with RO·, few reliable measurements of the temperature dependence of autoxidation reactions are available because of the increasing complexity associated with increasing temperature and the failure of simple kinetic expressions under these conditions. Where available [9], such data support the idea that abstractions of alkanes by $RO_2\cdot$ have values of log $(A/M^{-1}s^{-1}) > 9$ [9, 10, and 11]. Therefore we have preassigned log A in order to calculate E from k on the same basis as for reactions of other radicals (table 1.1). In the few cases where reliable temperature dependent measurements are available from which to estimate log A and E, these values are also noted in the tables.

Two kinds of absolute rate data are available for many autoxidation systems owing to the extensive use of the added hydroperoxide technique. First are values of k for $RO_2\cdot + RH$, and second are values of k' for t-$BuO_2\cdot + RH$. Use of k' alone is advantageous in calculating relative reactivities of substrates and provides absolute values that are intercomparable among many substrates. The tables 6.1 through 6.10 provide both k and k', but A' and E' have been assigned and calculated only for values of k'.

Recent measurements of absolute rate constants for H-atom transfer to $RO_2\cdot$ radicals for a wide variety of hydrocarbons, olefins, and functionalized organic compounds [9] suggest that good correlations exist between log k or log k' and C—H bond strengths (D(R—H)). For primary and secondary $RO_2\cdot$ radicals the following relation holds at 303 K:

$$\log (k/M^{-1}s^{-1}) = 16.4 - 0.2(D[\mathrm{R—H}] + \Delta) \quad \text{(in kcal/mol)},$$

where Δ is a correction needed to place log k on the line defined by the equation. A similar equation holds for reactions of tertiary $RO_2\cdot$ radicals

$$\log (k/M^{-1}s^{-1}) = 15.4 - 0.2(D[\mathrm{R—H}]) + \Delta) \quad \text{(in kcal/mol)}.$$

For thirty functionalized compounds the average deviation, $\Delta = \pm 3$; for thirty alkanes and olefins, $\Delta = \pm 2$.

6.3. Error Analysis

We estimate that the probable error in k is $\pm 10\%$, the error in log A is ± 0.5 log units and the derivative error in E is 1 kcal/mol.

TABLE 6.1. Peroxy radicals-organic compounds: summary of absolute rate constants k for $RO_2\cdot + RH$, k' for t-$BuO_2\cdot + RH$ and rate parameters at 303 K per reactive hydrogen.

Substrate and position	$k/M^{-1}s^{-1}$	$k'/M^{-1}s^{-1}$	log $(A/M^{-1}s^{-1})$ [a]	E' [b] kJ/mole (kcal/mole)	
Alkyl					
primary					
secondary		0.00027	9.2	74.0	(17.7)
tertiary	0.0048	0.0048	9.4	67.9	(16.2)
cyclo		0.00027	9.2	74.0	(17.7)
Allyl					
primary	0.14				
secondary	0.50	0.084	8.2	53.8	(12.8)
tertiary	1.2				
cyclo	1.6	0.80	8.5	49.8	(11.9)
Benzyl					
primary	0.08	0.012	8.0	57.5	(13.7)
secondary	0.05	0.10	8.2	53.3	(12.7)
tertiary	0.18	0.16	8.4	53.3	(12.7)
cyclo	1.6	0.50	8.5	51.0	(12.2)
Acetylenic	0.7				
Dienes					
1,4	7.0	0.23	7.5	47.2	(11.3)
1,3	31.0				
cyclo 1,3	55	1.4	8.0	45.5	(10.9)
cyclo 1,4	370	20	8.5	41.7	(9.97)
Alcohols					
secondary		0.009	9.2	65.2	(15.6)
cyclo	0.036				
benzyl	2.4	0.065	8.0	38.5	(9.19)
Ethers					
secondary	0.3	0.016	9	62.6	(14.9)
tertiary	0.02	0.02	9	62.0	(14.8)
benzyl	5.8	0.55	8	41.9	(10.0)
cyclo sec 5 ring	1.1	0.085	8.7	56.6	(13.5)
cyclo tert 5 ring	2.4	0.4	8.7	52.7	(12.6)
cyclo 5 ring	0.14	0.006	8.7	63.3	(15.1)

[a] Assigned; see table 1.1.
[b] Calculated from k and log A'.

TABLE 6.2. Peroxy radicals-alkanes: absolute rate constant k for $RO_2\cdot + RH$, k' for t-$BuO_2\cdot + RH$ and rate parameters for k' per reactive hydrogen

Substrate and position	$k/M^{-1}s^{-1}$	Temp. K	Ref.	$k'/M^{-1}s^{-1}$ $\times 10^6$	Temp. K	log $(A'/M^{-1}s^{-1})$ [b]	E' [c] kJ/mol	(kcal/mol)	Ref.
n-Butane									
2-CH	0.0003	303	10						
Isobutane									
3-CH	0.005	303	11	5.0	3.3	8.8 [a]	69.9	(16.7) [a]	11
						9.4 [b]	67.8	(16.2) [c]	
2,4,6-Trimethylheptane									
3-CH	0.017	303	12						
Tridecane									
2-CH				0.27	303	9.4 [a]	74.4	(17.8) [a]	9
				0.86	313	9.2 [b]	74.0	(17.7) [c]	
Hexadecane									
2-CH				0.30	303	9.4 [a]	74.4	(17.8)	9
				0.92	313	9.2 [b]			
Cyclohexane									
2-CH	0.044	333	13	0.28	303	9.4 [a]	74.4	(17.8) [a]	9
				0.65	313	9.2 [b]	73.9	(17.7) [c]	

[a] Experimental value [9].
[b] Assigned; see table 1.1.
[c] Calculated from k' and log A'.

TABLE 6.3. Peroxy radicals-alkenes and polyenes: H-atom transfer from allylic positions; absolute rate constants k for $RO_2\cdot + RH$, k' for t-BuO_2 + RH at 303 K and rate parameters for k' per reactive hydrogen

Substrate	$k/M^{-1}s^{-1}$	Ref.	$k'/M^{-1}s^{-1}$	log $(A'/M^{-1}s^{-1})$ [a]	E' [b] kJ/mol	(kcal/mol)	Ref.
2,3-Dimethylbutene-2	0.14	9					
Cyclopentene	1.7	9	0.85	8.5	49.69	(11.87)	9
Cyclohexene	1.5	9	0.75	8.5	49.98	(11.94)	9
2,5-Dimethylhexene-3	1.2	9					
Heptene-3	0.35		0.05	8.2	55.09	(13.16)	9
Octene-1	0.50	9	0.084	7.1 [c]	47.13	(11.26) [c]	9
				8.2	53.53	(12.79)	
Decyne-5	0.70	9					
Pentadiene-1,4	7.0	9	0.23	7.5	47.18	(11.27)	
Cyclohexadiene-1,3	55	9	≥ 1.4	8.0	45.52	(10.88)	9, 16
Cyclohexadiene-1,4	370	9	20	8.5	41.72	(9.97)	9, 17
Methyl linoleate (octadecadieneoate)	31	9					
Methyl linolenate (octadecatrieneoate)	59	9					

[a] Assigned; see table 1.1.
[b] Calculated from k' and log A'.
[c] Experimental value 283–343 K.

TABLE 6.4. Peroxy radicals-aralkanes: H-atom transfer from benzyl CH; absolute rates constant k for $RO_2\cdot + RH$, k' for t-$BuO_2\cdot + RH$ at 303 K and rate parameters for k' at 303 K [9] per reactive hydrogen

Substrate	$k/M^{-1}s^{-1}$	$k'/M^{-1}s^{-1}$	log $(A'/M^{-1}s^{-1})$ [a]	E' [b] kJ/mol	(kcal/mol)
Toluene	0.08	0.012 [c]	8.0	57.51	(13.74)
o-Xylene	0.07				
m-Xylene	0.08				
p-Xylene	0.14	0.015	8.0	56.92	(13.60)
Ethylbenzene	0.65	0.1	8.2	53.32	(12.74)
n-Butylbenzene	0.28				
sec-Amylbenzene	0.07				
sec-Butylbenzene	0.08				
Cumene	0.18	0.16	8.4	53.28	(12.73)
Indan	1.2	0.37	8.5		
Tetralin	1.6	0.50	8.5		
Phenylcyclohexane	0.06				
Bibenzyl	0.14	0.045	8.2	55.33	(13.22)
Diphenylmethane	1.0	0.16			
1,1-Diphenylethane	0.44				
9,10-dihydroanthracene	80	6.0			

[a] Assigned; see table 1.1.
[b] Calculated from k' and log A'.
[c] Absolute values of k' for 13 meta- and para-substituted toluenes fit the equation $\log k' = -0.56\,\sigma^* - 2.0$ [14]; values of k for meta- and para-substituted cumenes toward cymylperoxy radical fit equation $\log k = -0.29\sigma^+ - 0.74$ [15].

TABLE 6.5. Peroxy radicals-aralkenes: H-atom transfer from benzyl-allyl CH: absolute rate constant k for $RO_2\cdot + RH$ at 303 K per reactive hydrogen [16]

Substrate	$k/M^{-1}s^{-1}$
Allylbenzene	5.0
Crotylbenzene	4.1
Indene	7.0
1,2-Dihydronaphthalene	26
1,4-Dihydronaphthalene (3-CH)	225

TABLE 6.6. Peroxy radicals-ketones: H-atom transfer at α-CH; absolute rate constant k for $RO_2\cdot + RH$ or k' for t-$BuO_2\cdot + RH$ at 303 K and rate parameters for k' per reactive hydrogen

Substrate, ketone	$k/M^{-1}s^{-1}$	log $(A'/M^{-1}s^{-1})$ [a]	E' [b] kJ/mol	(kcal/mol)	Ref
Methyl ethyl	0.055				17
Methyl n-propyl	0.0035				18
Methyl isopropyl	0.36				18
Diisopropyl	0.026 (k')	8.7	59.61	(14.24)	9
Dibenzyl	0.045 (k')	8.2	55.33	(13.22)	9
Cyclohexanone	0.19				19

[a] Assigned; see table 1.1.
[b] Calculated from k' and log A'.

TABLE 6.7. Peroxy radicals-aldehydes: H-atom transfer from acyl CH; absolute rate constants k for $RCO_3\cdot + RCHO$, [20] k' for t-$BuO_2\cdot + RCHO$ [21]

Substrate	$k/M^{-1}s^{-1}$	Ref.
Acetaldehyde	2700	20
Heptanal	3100	
Octanal	3900	
Decanal	2700 [a]	21
Pivaldehyde	2500	
Cyclohexane-carbaldehyde	1100	
Benzaldehyde	12 000	22
	0.85 (k') [b]	

[a] Measured at 278 K.
[b] This rate constant with assigned log $A' = 8.7$ gives $E = 50.84$ kJ/mol (12.14 kcal/mol).

TABLE 6.8. Peroxy radicals-alcohols and ethers: H-atom transfer at α-CH; absolute rate constant k for $RO_2\cdot + RH$, k' for t-$BuO_2\cdot + RH$ at 303 K and rate parameters for k' per reactive hydrogen

Substrate	$k/M^{-1}s^{-1}$	Ref.	$k'/M^{-1}s^{-1}$	log $(A'/M^{-1}s^{-1})$ [a]	E' [b] kJ/mol	(kcal/mol)	Ref.
Alcohols							
Cyclohexanol	0.17	23					
Benzyl alcohol	2.4	22	0.065	8.2	54.42	(13.00)	22
α-Methylbenzyl	2.1	22	0.10	8.4	54.49	(13.02)	22
Ethers							
Diisopropyl							
intermolecular	0.055	24	0.055	8.7	57.72	(13.79)	25
intramolecular	0.2–0.7						
Di-n-butyl	0.3	24	0.016	8.7	60.82	(14.53)	25
Isopropyl t-butyl	0.02		0.02	8.7	60.28	(14.40)	
Tetrahydrofuran	1.1		0.085	8.7	56.64	(13.53)	
Tetrahydropyran	0.14		0.006	8.7	63.29	(15.12)	
2,5-Dimethyltetrahydrofuran	2.4		0.4	8.7	52.74	(12.60)	
1,4-Dioxan	0.12						
Benzyl t-butyl	5.8		0.55	8.2	49.02	(11.71)	
Benzyl phenyl	0.75		0.10	8.2	53.32	(12.74)	
Dibenzyl							
intermolecular	7.5		0.32	8.2	50.40	(12.04)	
intramolecular	15.30						
Di-α-methylbenzyl			0.042	8.4	56.67	(13.54)	
Phthalan	108						

[a] Assigned; see table 1.1.
[b] Calculated from k' and log A'.

TABLE 6.9. Peroxy radical-organic sulfides: H-atom transfer from α-CH; absolute rate constant k for $RO_2\cdot + RH$, k' for t-$BuO_2\cdot + RH$ at 303 K and rate parameters for k' per reactive hydrogen [26]

Substrate, sulfide	$k/M^{-1}s^{-1}$	$k'/M^{-1}s^{-1}$	log $(A'/M^{-1}s^{-1})$ [a]	E' [b] kJ/mol	(kcal/mol)
Benzyl t-butyl		0.05	8.2	55.09	(13.16)
Benzyl phenyl	4.75	0.08	8.2	53.87	(12.87)
Dibenzyl		0.087	8.2	53.66	(12.82)
Tetrahydrothiophene	1.6	0.025	8.7	59.73	(14.27)
Tetrahydrothiopyran	0.37	0.005	8.7	63.75	(15.23)

[a] Assigned; see table 1.1.
[b] Calculated from k' and log A'.

TABLE 6.10. Peroxy radical-organic compounds; H-atom transfer adjacent to functional group; absolute rate constant k for $RO_2\cdot + RH$ and k' for t-$BuO_2\cdot + RH$ at 303 K and rate parameters for k' per reactive hydrogen [9]

Substrate	$k/M^{-1}s^{-1}$	$k'/M^{-1}s^{-1} \times 10^3$	log $(A'/M^{-1}s^{-1})$ [a]	E' [b] kJ/mol	(kcal/mol)
Isopropyl alcohol		9	8.7	62.29	(14.88)
Isopropyl acetate		2.4	8.7	65.59	(15.67)
2-Chloropropane		0.6	8.7	69.11	(16.51)
2-Bromopropane		0.6	8.7	69.11	(16.51)
2-Nitropropane		0.3	8.7	70.87	(16.93)
2-Cyanopropane		10	8.7	62.04	(14.82)
Methyl isobutyrate		12	8.7	61.58	(14.71)
Benzyl chloride	1.5	8	8.2	59.69	(14.26)
Benzyl bromide		6	8.2	60.40	(14.43)
Benzyl acetate	2.3	8	8.2	59.69	(14.26)
Benzyl benzoate	2.6	9	8.2	59.40	(14.19)
t-Butyl phenylacetate	0.8	30	8.2	56.34	(13.46)

[a] Assigned; see table 1.1.
[b] Calculated from k' and log A'.

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