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KINETIC DATA FOR HYDROGEN AND DEUTERIUM ATOM ABSTRACTION BY METHYL AND TRIFLUOROMETHYL RADICALS IN THE GASEOUS PHASE

P. GRAY,* A. A. HEROD,† AND A. JONES*,#

Physical Chemistry Department, University of Leeds, Leeds LS2 9JT, England

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Contents

I. Introduction

This review is concerned with reactions in which hydrogen and deuterium atoms are abstracted by methyl and trifluoromethyl radicals. They can be formally represented by the reactions

$$R + XH \longrightarrow RH + X$$
$$R + XD \longrightarrow RD + X$$

where R is methyl or trifluoromethyl and X is a free radical or atom. Measurements of reaction rates and Arrhenius parameters for these reactions are important since the reactions occur widely in processes of industrial importance and play major roles in many combustion and explosive processes.

A considerable amount of data has accumulated over the past twenty years concerning these reactions; indeed, a recent compilation[1] showed that there are now quantitative kinetic data available for more methyl radical reactions than for any other free radical or atom. However, much of this work, and particularly the earlier studies, failed to isolate individual re-

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* Address correspondence to these authors.

† Present address: B.C.U.R.A. Industrial Laboratories, Randalls Road, Leatherhead, Surrey, England.

Present address: Ministry of Technology, S.M.R.E., Sheffield S3 7HQ, England.

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actions with the result that rate data for simultaneous, composite reactions were obtained. Arrhenius parameters derived from such rate measurements have no simple physical significance and relationships shown by these reactions are obscured. Now that the techniques of isotopic labeling have been applied to these systems, it is possible to isolate many primary reactions, and so obtain unambiguous kinetic data. In the recent past, many systems have been investigated in this way, and this present situation provides an opportunity for their survey and an examination of possible theoretical models.

Accordingly, it is the aim of this review to summarize, assess, and correlate as many as possible of the available data (up to early 1970) for the individual reactions of methyl and trifluoromethyl radicals in the gaseous phase. In addition, it aims to consider kinetic data calculated for the reverse reactions, and to examine data on gas-phase isotope effects that have emerged from the labeling experiments in the light of current theories of isotope effects. Throughout the review we have restricted ourselves to gas-phase reactions.

The units adopted for the second-order rate constants are $cm^3\ mol^{-1}\ sec^{-1}$ because they are the most commonly used among practising reaction kineticists in this field. To convert such units to others occasionally encountered, the following relationships are required: $k\ cm^3\ mol^{-1}\ sec^{-1} = 10^3k\ l.\ mol^{-1}\ sec^{-1} = 10^6k\ m^3\ mol^{-1}\ sec^{-1} = 1.7 \times 10^{-24}k\ cm^3\ molecule^{-1}\ sec^{-1}$.

For rate constants to be compared, a common temperature for all comparisons is a considerable convenience. In the past, 182°C (455 K) and 164°C (437 K) have both been used. We have chosen the latter as it more often lies within the experimental range studied; more trivially it also offers the convenience that $2.303RT$ is 2 kcal mol^{-1}, so that

$$\log k\ (164°) = \log A - E/2\ \text{kcal mol}^{-1}$$

All kinetic data have been expressed in terms of the simple Arrhenius equation $k = Ae^{-E/RT}$. Where rate constants have appeared in the form $k = A'T^{1/2}e^{-E'/RT}$ in the original papers, conversion to simple Arrhenius parameters has been made using the relationships $A = A'e^{1/2}T^{1/2}$ and $E = E' + {}^1/_2RT$.

II. Experimental Methods

A. FREE RADICAL SOURCES

The generation of methyl and trifluoromethyl radicals has been the subject of much discussion,[2,3] and it is the intention here simply to present the different sources that have been used and to give their salient features, emphasizing the more recent developments.

1. Methyl Radical Sources

Methyl radicals can be produced thermally or photolytically. The following compounds have been used as thermal sources: di-*tert*-butyl peroxide,[4–7] dimethylmercury,[8–12] dimethylcadium,[9–11] dimethylzinc,[11,13] trimethylbismuth,[11,14] trimethylantimony,[11,14] $SnMe_2Cl_2$,[11,14] methylsilver, tetramethylsilane, tetramethyllead, tetramethyltin, trimethylarsine,[10] and acetaldehyde.[15–17]

Thermal production of methyl radicals suffers from the disadvantage that the necessary decompositions have substantial activation energies so that the temperature ranges over which they can be used are limited. Di-*tert*-butyl peroxide, in many respects the best pyrolytic source, requires an activation energy[4] of 38 kcal mol^{-1} and is normally suitable as a source of methyl radicals only in the temperature range 130–170°, though it may be used[18,19] at higher temperatures in flow systems.

The following compounds have been used as photolytic sources of methyl radicals: acetone,[2,20–24] acetone-d_6,[2,21,23,24] azomethane,[2,25–27] azomethane-d_6,[26,28] dimethylmercury,[29] acetaldehyde,[30–33] ketene,[34] biacetyl,[35,36] and methyl iodide.[8]

Photolytic sources have the advantage that larger temperature ranges may be used since the rate of production of radicals depends on the incident light intensity which can be varied. In addition, the photolytic decompositions may be carried out at lower temperatures than the pyrolyses, leading in general to simpler mechanisms.

Of the compounds listed above, the most frequently used photolytic sources are acetone and azomethane. Acetone is the most convenient source of methyl or trideuterimethyl radicals since acetone and acetone-d_6 are readily available and thermally stable over a useful temperature range of 120–300°. Their photolyses are well understood, and the production of CO serves as an internal actimometer. Azomethane (useful temperature range 70–200°) is less convenient than acetone because it is a gas at room temperature and is unstable to

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ordinary light. It has two advantages over acetone. (a) Methyl radicals attack azomethane faster than acetone; hence this reaction may be used as the reference reaction for attack on deuterated compounds such as D_2S, where very little dimerization to ethane might occur. (b) Whereas acetone is known to react with amines in the liquid phase and may do so slowly in the vapor phase, azomethane has no such reaction.

Of the other photolytic sources, acetaldehyde does not offer a simple decomposition, and methyl iodide photolysis is accompanied by the formation of iodine atoms which scavenge radicals. The primary steps in the photolysis of carbonyl compounds have been reviewed.[37]

2. *Trifluoromethyl Radical Sources*

Trifluoromethyl radicals may be produced both thermally and photolytically. Although trifluoroacetaldehyde (CF_3CHO),[38] hexafluoroazomethane,[39,40] and perfluorotetramethylsilver[41] have been used, thermal sources have found little use in CF_3 radical work. In the case of CF_3CHO, much trifluoromethane is produced by attack on the radical source, and a radical-chain mechanism is involved. Hexafluoroazomethane has found some use[39] in the pyrolytic decomposition, but only to confirm that the pyrolysis and photolysis gave identical results.

The most convenient and widely used trifluoromethyl radical sources are photolytic. They are hexafluoroacetone,[42-46] hexafluoroazomethane,[19,39,47,48] trifluoroacetaldehyde,[49] trifluoromethyl iodide,[50-52] and perfluorodimethylmercury.[53]

Of the sources listed, hexafluoroacetone is the most common because it is both relatively cheap and readily available. While it is a convenient source for use with hydrocarbons, ethers, and tertiary amines, it is not suitable for alcohols or primary and secondary amines because it undergoes condensations with them. The photolysis of CF_3I has been used recently[51] to overcome this problem.

B. COMPETITIVE METHODS FOR MEASURING RATE CONSTANTS

For reactions of the type

$$R + XH \longrightarrow RH + X \tag{1}$$

where R is a methyl or trifluoromethyl radical, the rate of the reaction is given by the expression

$$\mathcal{R}_1 = k_1[R][XH] \tag{i}$$

where [R] and [XH] are the concentrations of the radical species and the reactant, respectively. Thus, the velocity constant k_1 can be calculated by measuring the rate of the reaction and the concentrations [R] and [XH]. Normally $\mathcal{R}_1$ and [XH] can be readily measured, but, in general, the concentration of radicals [R] is inaccessible. It can, however, be determined indirectly by following a suitable competitive reaction. Thus, if the reaction

$$R + E \longrightarrow F \tag{2}$$

in which E is a reactant and F some distinctive product, takes place simultaneously with reaction 1, then the rate of this reaction is given by the equation

$$\mathcal{R}_2 = k_2[R][E] \tag{ii}$$

Since [R] refers to the same concentration in both cases, combination of eq i and ii gives the expression

$$k_1/k_2 = \mathcal{R}_1[E]/\mathcal{R}_2[XH] \tag{iii}$$

and the ratio k_1/k_2 can thus be determined by measuring the rates $\mathcal{R}_1$ and $\mathcal{R}_2$ and the concentrations [E] and [XH]. The rates are usually obtained by measuring rates of production of the distinguishable products RH and F, and the concentrations can be maintained effectively constant throughout a run by working to a few per cent decomposition only. Knowing the value of k_1/k_2, k_1 can be obtained providing the value of k_2 is known.

The choice of the reference reaction is determined by the reaction under investigation. Two separate approaches can be distinguished. In the first, the reactant in the reference reaction is deliberately added to the reaction system. This approach has been used[19] in studying reactions between trifluoromethyl radicals and hydrocarbons of the type

$$CF_3 + XH \longrightarrow CF_3H + X \tag{3}$$

Deuterium was added to the system so that the reaction

$$CF_3 + D_2 \longrightarrow CF_3D + D \tag{4}$$

could be used as a reference reaction. The value of k_3/k_4 was then determined by applying eq iii, which took the form

$$k_3/k_4 = \mathcal{R}_{CF_3H}[D_2]/\mathcal{R}_{CF_3D}[XH] \tag{iv}$$

Values of k_3 for a series of hydrocarbons can then be evaluated using the known value of k_4.

In the second approach, which is often more convenient for investigating the abstraction of hydrogen atoms by methyl radicals, one of the reactions naturally occurring in the reaction system is employed as the reference reaction. Two such methods have been widely used.

Method 1 involves the production of methyl-d_3 radicals, usually by the photolysis of acetone-d_6. When acetone-d_6 is photolyzed above 120° in the presence of a substrate XH, the following reactions take place.

$$CD_3COCD_3 \xrightarrow{h\nu} 2CD_3 + CO \tag{5}$$

$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3 \tag{6}$$

$$CD_3 + XH \longrightarrow CD_3H + X \tag{7}$$

$$2CD_3 \longrightarrow C_2D_6 \tag{8}$$

Using reaction 6 as the reference reaction, the quotient of

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velocity constants (k_7/k_6) can be obtained by application of eq iii which now becomes

$$k_7/k_6 = \mathcal{R}_{\mathrm{CD_3H}}[\mathrm{CD_3COCD_3}]/\mathcal{R}_{\mathrm{CD_4}}[\mathrm{XH}] \qquad \text{(v)}$$

Since the quantities on the right-hand side of the equation are all readily obtained experimentally, and the "absolute" value of k_6 is known, k_7 can be calculated.

Method 2 is more general in that it employs the dimerization of methyl radicals as the reference reaction. It can be illustrated by the reactions occurring during the photolysis of azomethane. Between 60 and 190°, the following reactions account for the products observed.

$$\mathrm{CH_3N_2CH_3} \xrightarrow{h\nu} \mathrm{2CH_3 + N_2} \qquad (9)$$

$$\mathrm{CH_3 + CH_3N_2CH_3} \longrightarrow \mathrm{CH_4 + CH_2N_2CH_3} \qquad (10)$$

$$\mathrm{2CH_3} \longrightarrow \mathrm{C_2H_6} \qquad (11)$$

The rate constant of reaction 10 can be determined relative to the rate constant for the combination of methyl radicals, reaction 11, by application of eq iii which now takes the form

$$k_{10}/k_{11}^{1/2} = \mathcal{R}_{\mathrm{CH_4}}/\mathcal{R}_{\mathrm{C_2H_6}}^{1/2}[\mathrm{CH_3N_2CH_3}] \qquad \text{(vi)}$$

The concentration of azomethane and the rate of production of methane and ethane can be readily measured, enabling the rate constant ratio $k_{10}/k_{11}^{1/2}$ to be evaluated. Since the rate constant for the combination of methyl radicals has been determined (see below), the rate constant k_{10} can be obtained.

If azomethane is photolyzed in the presence of a substrate XH, the reaction

$$\mathrm{CH_3 + XH} \longrightarrow \mathrm{CH_4 + X} \qquad (12)$$

must be added to the previous scheme (reactions 9–11) for azomethane photolysis. The rate constant of reaction 12 can be obtained relative to the velocity constant k_{11}, as before, by using the equation

$$k_{12}/k_{11}^{1/2} = \mathcal{R}_{\mathrm{CH_4}}(12)/\mathcal{R}_{\mathrm{C_2H_6}}^{1/2}[\mathrm{XH}] \qquad \text{(vii)}$$

where $\mathcal{R}_{\mathrm{CH_4}}(12)$, the rate of methane production by reaction 12, is given by the relation

$$\mathcal{R}_{\mathrm{CH_4}}(12) = \mathcal{R}_{\mathrm{CH_4}}^{\mathrm{total}} - (k_{10}/k_{11}^{1/2})\mathcal{R}_{\mathrm{C_2H_6}}^{1/2}[\mathrm{CH_3N_2CH_3}] \qquad \text{(viii)}$$

The method is further applicable to the abstraction of deuterium atoms from the compound X–D. When azomethane is photolyzed in the presence of XD, the reaction

$$\mathrm{CH_3 + XD} \longrightarrow \mathrm{CH_3D + X} \qquad (13)$$

is added to the scheme for azomethane photolysis. In this case, the only source of CH_3D is that produced by reaction 13, and the ratio of rate constants may be expressed as

$$k_{13}/k_{11}^{1/2} = \mathcal{R}_{\mathrm{CH_3D}}/\mathcal{R}_{\mathrm{C_2H_6}}^{1/2}[\mathrm{XD}] \qquad \text{(ix)}$$

1. *Reference Reactions*

The rate constant for the dimerization of methyl radicals is of great importance because of the large number of rate constants determined relative to it. Accordingly, a number of attempts have been made to determine its absolute value and are listed elsewhere.[54] The most reliable of these values appear to be those of Gomer and Kistiakowsky[55] and Kistiakowsky and Roberts[56] using the rotating sector technique. After developing a more refined rotating sector theory, Shepp[57] recalculated the results of these two studies and proposed as the value for the rate constant

$$k\ (\mathrm{cm^3\ mol^{-1}\ sec^{-1}}) = 10^{13.34} \exp\{-[(0 \pm 700\ \mathrm{cal})/RT]\}$$

It is this value which is currently accepted. Although the expression was obtained over the temperature range 125–175°, investigators have relied on its validity over much greater temperature ranges. A recent determination[58] using flash photolysis gave a value, at 20°, for the rate constant of $10^{13.39\pm0.04}$ $\mathrm{cm^3\ mol^{-1}\ sec^{-1}}$, in good agreement with Shepp's value.

For the reaction

$$\mathrm{CD_3 + CD_3COCD_3} \longrightarrow \mathrm{CD_4 + CD_2COCD_3}$$

the following rate expression is considered the most reliable.

$$k\ (\mathrm{cm^3\ mol^{-1}\ sec^{-1}}) = 10^{11.6} \exp[-(11.4\ \mathrm{kcal}/RT)]$$

For the dimerization of trifluoromethyl radicals, Ayscough's value[59] of k ($\mathrm{cm^3\ mol^{-1}\ sec^{-1}}$) = $10^{13.36}$ is generally accepted. A recent study[60] of the flash photolysis of trifluoromethyl iodide produced values for the rate constant, at 25°, which varied between $10^{12.8}$ and $10^{13.0}$ $\mathrm{cm^3\ mol^{-1}\ sec^{-1}}$.

C. ISOTOPIC TECHNIQUES

The general method of isotopic labeling used in the reactions described here may be illustrated by consideration of the methyl radical attack on methylamine.

The rate constants for attack on the different sites in the four isotopically substituted methylamines can be represented as follows.

CH_3NH_2	CD_3NH_2	CH_3ND_2	CD_3ND_2
$k_1\ k_2$	$k_1'\ k_2'$	$k_1''\ k_2''$	$k_1'''\ k_2'''$

Determinations of the rate of production of CH_4, using azomethane or acetone as the methyl radical source and CH_3NH_2 as substrate, give values for $k_1 + k_2$.

By using CD_3NH_2 as the substrate, the rate constants k_1' and k_2' can be obtained separately since measurements of CD_4 production will result in the determination of k_1'. From work with CD_3ND_2, only the sum $k_1''' + k_2'''$ can be found.

The assumption that secondary isotope effects are zero (*i.e.*, that isotopic substitution at a site not involved in the reaction does not affect the rate of the reaction) enables k_1 and k_2 to be obtained from a study of CH_3NH_2 and either CD_3NH_2 or CH_3ND_2 since the following equalities then apply: $k_1 = k_1''$, $k_1' = k_1'''$, $k_2 = k_2'$, $k_2'' = k_2'''$. Secondary isotope effects are always small,[61] and when measurements were made[25] on the three isotopic species CH_3NH_2, CD_3NH_2, and CH_3ND_2, they were shown to be smaller than the experimental error by a factor of 50.

Because of corrections that have to be made to the rates of methane production to allow for attack on the radical source, it is necessary to choose the best combination of isotopic radi-

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cal source and substrate. For example, when methyl radical attack on the substrate is slow, the methane formed by attack on the radical source can be diminished by using acetone-d_6 or azomethane-d_6 and so favor attack on the substrate. The methyl radical attack on ethylenimine has been investigated using two isotopically different systems, $CH_3 + (CH_2)_2ND$ and $CD_3 + (CD_2)_2NH$. It is instructive to note that, since attack is mainly at the imine group, the system which would result in the most precise rate constants for attack on the methylene groups ($CD_3 + (CH_2)_2ND$) remains to be investigated.

D. COMPLICATIONS

The first essential in these studies is to establish the correct mechanism for the photolysis or pyrolysis of the radical source. For many of the common free radical sources, this is not difficult, though some doubt has recently been expressed[62–65] about the use of hexafluoroacetone as a photolytic source of CF_3 radicals.

Another essential is to ensure the compatibility of the radical source and substrate. The condensation of some amines with acetone is an obvious example of incompatible pairs, but a more subtle example (which probably invalidates earlier work) was found during an investigation of the methyl radical attack on methanol. In this study[66] it was found that an isotopic exchange reaction between acetone and the alcoholic hydroxyl group made it necessary to restrict work to the isotopically compatible systems $CH_3COCH_3 + CD_3OH$ and $CD_3COCD_3 + CH_3OD$.

Undoubtedly a major complication can be the role of secondary radical reactions. The previous analysis deduces quotients of rate constants from rates of production of methane and ethane. If methane or ethane arise from any reactions other than those formulated, then the treatment is invalidated. One example is afforded by methyl radical attack on formamide.[67,68] Primary attack favors the formyl hydrogen atom, and it might be thought that by using $HCONH_2$ and $DCONH_2$ as substrates, attack at the NH_2 group could be easily distinguished. However the radical $CONH_2$ produced by the primary attack contains a very labile hydrogen atom which is lost at any collision with CH_3.

$$CONH_2 + CH_3 \longrightarrow HNCO + CH_4$$

Thus instead of deriving rate constants for each site in the molecule, composite rate constants, reflecting contributions from secondary attack, are obtained. At present it is only possible to estimate attack at the NH_2 site in formamide from data obtained from acetamide.

Another example[66] is to be found in the methyl-d_3 radical attack on 2-propanol-d_1 where the methyl-d_3 radical undergoes a disproportionation reaction with the radical produced by primary attack.

$$CD_3 + (CH_3)_2COD \longrightarrow CD_4 + (CH_3)_2CO$$

A different type of interference arises from radical displacement reactions such as

$$CD_3 + CH_3R \longrightarrow CH_3 + CD_3R$$

where CH_3R is a molecule or free radical. Reactions of this kind have been observed in the methyl-d_3 radical attack on methylmercaptan[69] and dimethylmercury.[70] Corresponding reactions have been detected in the methyl radical attack on hexafluoroacetone,[71] hexafluoroazomethane,[72] and halogenated methanes.[73,74]

Radical displacement reactions of the type

$$CH_3 + CH_3R \longrightarrow C_2H_6 + R$$

where CH_3R is a molecule or free radical, have been postulated as sources of possible interference. Examples of this type of reaction are to be found in the photolysis of azomethane[27] and in the pyrolysis of hexafluoroazomethane.[39]

III. *Elementary Theoretical Considerations*

Before the results of experimental investigations are presented, it is convenient to consider what common features are to be expected. We deal here with the possibilities of predicting activation energies and preexponential factors, with the relationships between the kinetics of forward and reverse reactions, and with bond dissociation energies. Section C assesses the significance of "experimental" Arrhenius parameters derived from measurements of a composite rate constant for simultaneous hydrogen abstraction from different sites in the same molecule.

A. THERMODYNAMIC ASPECTS OF HYDROGEN ABSTRACTION

1. *Bond Dissociation Energy, Activation Energy, and Enthalpy Changes*

In all the reactions reviewed here, one bond is broken and another formed.

$$R + X\text{-}H \longrightarrow R\text{-}H + X \qquad (14)$$

$$\Delta H = D(X\text{-}H) - D(R\text{-}H) = E_f - E_r$$

The overall enthalpy increase accompanying the reaction is thus the difference in bond dissociation energies, and the relative strengths of the bond X–H in the substrate and the bond R–H in methane or trifluoromethane determine whether the reaction is endothermic (ΔH positive) or exothermic (ΔH negative). These bond dissociation energies $D(R\text{-}H)$ are high. In methane $D(CH_3\text{-}H)$ is 104 kcal mol^{-1} and in trifluoromethane $D(CF_3\text{-}H)$ is 106 kcal mol^{-1}. Values for the deuterated anaogs[75] are higher by about 1.2 kcal mol^{-1}, the zero-point energy difference.

Values for bond dissociation energies $D(X\text{-}H)$ in different substrates are collected for convenience in Appendix II. Wherever possible they match those of Kerr's[76] recent review although attention is drawn to particular exceptions. Not many organic compounds have higher bond dissociation en-

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(62) A. Gandini, D. A. Whytock, and K. O. Kutschke, *Proc. Roy. Soc., Ser. A*, **306**, 503, 511, 529, 537, 541 (1968), and references therein.

(63) N. C. Long and K. O. Kutschke, *Can. J. Chem.*, **46**, 1031 (1968).

(64) J. S. E. McIntosh and G. B. Porter, *J. Chem. Phys.*, **48**, 5475 (1968).

(65) L. M. Quick and E. Whittle, *Can. J. Chem.*, **45**, 1902 (1967).

(66) P. Gray and A. A. Herod, *Trans. Faraday Soc.*, **64**, 2723 (1968).

(67) J. C. Boden and R. A. Back, *ibid.*, **66**, 175 (1970).

(68) P. Gray and L. J. Leyshon, *ibid.*, **65**, 780 (1969).

(69) G. Greig and J. C. J. Thynne, *ibid.*, **62**, 379 (1966).

(70) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **86**, 2068 (1964).

(71) R. D. Giles and E. Whittle, *Trans. Faraday Soc.*, **61**, 1425 (1965).

(72) L. Batt and J. M. Pearson, *Chem. Commun.*, 575 (1965).

(73) K. D. King and E. J. Swinbourne, *J. Phys. Chem.*, **71**, 2371 (1967).

(74) D. M. Tompkinson and H. O. Pritchard, *ibid.*, 70, 1579 (1966).

(75) C. C. Robinson, S. A. Tare, and H. W. Thompson, *Proc. Roy. Soc., Ser. A*, **269**, 492 (1962).

(76) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

ergies than methane: notable exceptions are benzene, ethylene, and acetylene and the carboxylic hydrogen of the acids. Other strong bonds include those in water and hydrogen cyanide.

The activation energies for forward and reverse reactions also differ by $\Delta H = D(\text{X–H}) - D(\text{R–H})$. No abstractions are known for which an activation energy is less than zero, and the relationship for an endothermic abstraction

$$E_f - E_r = \Delta H > 0$$

thus sets a lower limit to E_f equal to the endothermicity. This relationship is of limited value, though its converse may be of use in placing bounds on bond dissociation energies. When experimental values for both E_f and E_r are available, unknown bond dissociation energies may be fixed in terms of known ones.

Empirical correlations between activation energies and enthalpies of reaction are another matter. Relationships between the two, first considered by Polanyi, have their uses but can be misleading when applied outside their context. They are best for interpolation in a homologous series and worst for transferring information from one bond type to another.

2. *Entropy Changes and Preexponential Factors*

The preexponential factors A_f and A_r for an abstraction reaction and its reverse are related to the overall entropy change by the expression

$$\log (A_f/A_r) = \Delta S^\circ/2.303R$$

The superscript in ΔS° normally denotes a standard state consistent with the units employed for the A factors; the consideration is unimportant for ideal gas reactions involving no change in mole numbers. It is strictly satisfied only if the A and E of the Arrhenius expression for velocity constant A exp($-E/RT$) are defined by the two relationships

$$E = RT^2 \, \mathrm{d} \ln k/\mathrm{d}T$$

$$A = \mathrm{d}(T \ln k)/\mathrm{d}T$$

3. *Prediction of Arrhenius Parameters and Velocity Constants for Reverse Reactions*

By combining the information sketched in the preceding sections, the relationship

$$k_f/k_r = A_f/A_r \exp(-E_f + E_r)/RT$$

may be exploited to yield information about a reaction from knowledge of the rate constant of the reverse reaction and the overall thermodynamics. This approach is often the only guide to many uninvestigated or inaccessible reactions and Appendix II exemplifies its use and scope. From many experimental studies of methyl radical reactions, predictions are there made about the vulnerability of methane to free radical attack by many other species.

B. TRANSITION STATE THEORY AND THE *A PRIORI* PREDICTION OF *A* FACTORS

It is still impossible to predict accurate activation energies for reactions of this family with confidence, although repeated and varied quantum mechanical attacks continue to raise fresh hopes. The situation is brighter for A factors, although numerous simplifying assumptions are always necessary and the calculations in practice are based less on first principles than is sometimes claimed.

1. *Calculations Based on the Detailed Specification of an Activated Complex*

A factors are calculated from the expression

$$A = (kT/h) \exp((\Delta S_c^{\ddagger}/R) + \Delta n^{\ddagger} + 1)$$

where k is Boltzmann's constant and h is Plank's constant. At 164°, (kT/h) is close to 10^{13} sec^{-1}. The entropy change $\Delta S_c^{\ddagger}$ refers to the formation of 1 mol of activated complex from $(1 + \Delta n^{\ddagger})$ mol of reactant, initial and final standard states being at unit concentration, and is a negative quantity. Its numerical value is related to $\Delta S^{\ddagger}$, the standard entropy change at a constant pressure of 1 atm, by the equation

$$\Delta S_c^{\ddagger} = (20.1\Delta n^{\ddagger} + \Delta S^{\ddagger}) \text{ cal mol}^{-1} \text{ deg}^{-1}$$

For the bimolecular reactions considered here, $(\Delta n^{\ddagger} + 1)$ is 2 and so log A is $15.3 + \Delta S + \Delta S^{\ddagger}/4.6$; the values of $\Delta S^{\ddagger}$ are characteristically around -20 cal deg^{-1} mol^{-1} and hence values of A are around 10^{11} cm^3 mol^{-1} sec^{-1}.

The problem is reduced to estimating $\Delta S^{\ddagger}$. Drastic assumptions are often made and values for $\Delta S^{\ddagger}$ frequently based on estimates of the overall entropy change ΔS. It is thus unwise to place much faith in the particular estimates of A factors obtained in this way. Values of $\Delta S^{\ddagger}$ taken as equal to or less than ΔS can be taken as lower limits. For a typical example log A for, say, methyl abstraction from ammonia is calculated as $10^{11.0}$ cm^3 mol^{-1} sec^{-1}.

2. *Calculations Based on Analogy*

The conceptual framework offered by transition state theory is perhaps its chief contribution, since the calculations attempted above require knowledge more detailed than we actually have. There are, however, a sufficient number of "experimentally measured" A factors for abstraction reactions by methyl and trifluoromethyl radicals for arguments based on analogy to be the safest prediction of all within the homologous series. For the great majority of abstractions from carbon–hydrogen bonds, A factors lie in the range $10^{10.5}$–$10^{11.5}$ cm^3 mol^{-1} sec^{-1}, and a guess that an unknown A is 10^{11} cm^3 mol^{-1} sec^{-1} is often borne out by subsequent work.

There are important exceptions: (a) reactions with molecular hydrogen (or deuterium) appear to have higher values for A, say 10^{12} cm^3 mol^{-1} sec^{-1}, a fact which can be rationalized readily by the theory above; (b) some reactions with amines have lower values for A, say 10^{10} cm^3 mol^{-1} sec^{-1}. This can be rationalized only by special assumptions about the activated complex. The value of transition state theory is that it focusses attention sharply on points of special interest and indicates the need for broadening the base of experiment.

Special interest attaches to (1) A factors for CH_3 and CF_3 abstractions and (2) A factors for isotopic pairs. These points are the subject of discussion in sections X and XI, respectively.

C. APPARENT ARRHENIUS PARAMETERS FOR SIMULTANEOUS REACTIONS

In compounds where abstraction can occur at two or more sites, the "experimental" velocity constant is the sum of two or

Table I

Abstraction of Hydrogen and Deuterium Atoms by Methyl Radicals from H_2, HD, and D_2

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k^a (cm³ mol⁻¹ sec⁻¹)*		*Ref*
					Overall	*Per atom*	
H_2	Acetone	130–290	11.5	10.0	6.5	6.2	21, 24, 80
H_2	$Hg(CH_3)_2$	25–250	11.7	9.9	6.7	6.4	24, 31
H_2	Acetone	136–318	11.7	10.5	6.5	6.2	82, 83
H_2	Ketene	99–207	11.5	10.2	6.4	6.1	34
H_2	Acetone-d_6	130–290	11.7	10.2	6.6	6.3	21, 80
H_2	Acetone-d_6	150–300	12.0	11.1	6.4	6.1	24
*H*D	Acetone	140–296	11.1	10.0	6.1	6.1	24
*H*D	Acetone-d_6	137–298	11.4	10.7	6.0	6.0	24
H*D*	Acetone	140–296	11.3	11.1	5.8	5.8	24
H*D*	Acetone	135–296	11.5	11.3	5.8	5.8	24
H*D*	Acetone-d_6	137–299	11.2	10.7	5.8	5.8	24
D_2	Acetone-d_6	130–290	11.4	10.9	5.9	5.6	21, 80
D_2	Acetone	140–425	11.5	11.9	5.6	5.3	85
D_2	Acetone	151–299	11.79	12.1	5.7	5.4	84
D_2	$Hg(CH_3)_2$	27–253	12.3	12.7	5.9	5.6	86
D_2	Acetone	150–458	11.7	12.2	5.6	5.3	82, 83
D_2	CH_3CHO	258–451	12.8	13.7	6.0	5.7	82, 83
D_2	Acetone	135–295	11.7	11.7	5.9	5.6	21, 24, 80
D_2	Acetone	130–290	11.8	11.8	5.9	5.6	24

[a] At 164°.

more velocity constants for elementary reactions, and, although each individually should follow a linear Arrhenius relationship, it is not to be expected that the overall velocity constant will behave in the same way. Cafferata, Kerr, and Trotman-Dickenson[77] have taken the view that the lack of significant curvature in Arrhenius plots for such reactions indicates either the exclusive occurrence of abstraction from one site or the identity of activation energies in the individual reactions. Gray and Herod[78] have considered the case of attack at two sites in a molecule (with $E_1 > E_2$ and $A_1 > A_2$) for which

$$k = (k_1 + k_2) = A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT)$$

Their analysis shows that an Arrhenius plot of $R \ln k$ *vs.* $1/T$ will have a slope E which is not strictly constant, but which in principle increases from a value near E_2 at low temperatures to a value near E_1 at high temperatures

$$\frac{\mathrm{d}E}{\mathrm{d}(RT^{-1})} = \left(\frac{\Delta E}{2R}\right)^2 \operatorname{sech}^2 \left[\frac{\Delta E}{2R}\left(\frac{1}{T^*} - \frac{1}{T}\right)\right]$$

where T^* is that temperature ("isokinetic") at which $k_1 = k_2$. Except for great differences in E, a very large temperature range is necessary to reveal the curvature. Even a 100° range and zero experimental error would reveal only a 1 kcal mol⁻¹ change in E for a realistic case where $E_1 = 9$ kcal mol⁻¹, $A_1 = 10^{11}$ cm³ mol⁻¹ sec⁻¹, $E_2 = 6$ kcal mol⁻¹, and $A_2 = 10^9$ cm³ mol⁻¹ sec⁻¹.

It is thus not simply a question of preference to employ isotopic labeling to study simultaneous reactions; it is inescapable if reliable results are to be determined.

IV. Abstraction from H_2, HD, and D_2

A. ATTACK BY METHYL RADICALS

All the experiments with methyl radicals were performed in the early 1950's, and it is rather surprising that they have not been repeated since, especially since many of them have been criticized subsequently. Some of the work has been reviewed by Walker[79] in connection with the equilibrium

$$H + CH_4 \rightleftharpoons CH_3 + H_2$$

The reactions of CH_3 (or CD_3) radicals with H_2, D_2, and HD are here discussed in turn.

1. Attack on H_2

Of the several investigations, the photolysis[24] of acetone-d_6 in the presence of H_2 seems the most reliable. Using mass spectrometric analysis of CD_4–CD_3H mixtures and methyl radical dimerization as the reference reaction, a rate constant of $10^{6.47}$ cm³ mol⁻¹ sec⁻¹ at 164° was obtained with an activation energy of 11.1 kcal mol⁻¹ and an A factor of $10^{12.0}$ cm³ mol⁻¹ sec⁻¹. A second method of estimating the methane (CD_3H) formed by CD_3 attack on H_2 (subtraction of the methane (CD_4) formed by CD_3 attack on the radical source from the total methane, CD_4 and CD_3H) led to a slightly higher rate constant, $10^{6.58}$ cm³ mol⁻¹ sec⁻¹ at 164°, but a markedly lower activation energy, 10.2 kcal mol⁻¹, and A factor, $10^{11.7}$ cm³ mol⁻¹ sec⁻¹. This alternative method of analysis of the methane formed is not likely to be as accurate as the first.

Of the other investigations of the reaction, many have been criticized and recalculated since their original publication, and they present a confused picture. The results are presented in Table I; the main points of agreement among the results for attack on H_2 are the values for the rate constant, the extremes

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(77) L. F. R. Cafferata, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1386 (1965).

(78) P. Gray and A. A. Herod, *Trans. Faraday Soc.*, **63**, 2489 (1967).

(79) R. W. Walker, *J. Chem. Soc. A*, 2391 (1968).

being $10^{6.4}$ and $10^{6.7}$ cm^3 mol^{-1} sec^{-1} at 164°. The activation energies, however, vary by more than 1 kcal mol^{-1}, while the A factors vary by a factor of 3. These investigations are now discussed and the reasons for discarding them given.

Majury and Steacie[21,80] photolyzed acetone and H_2 mixtures and found a rate constant at 164° of $10^{6.5}$ cm^3 mol^{-1} sec^{-1} with an activation energy of 9.2 kcal mol^{-1} and an A factor of $10^{11.1}$ cm^3 mol^{-1} sec^{-1}. Whittle and Steacie[24] consider that the activation energy should be nearer 10 kcal mol^{-1} since in their own work activation energies low by 1 kcal mol^{-1} resulted[24] from applying Majury and Steacie's[21,80] methods of calculation.

Majury and Steacie[21,80] also photolyzed mixtures of acetone-d_6 and H_2, obtaining a rate constant at 164° of $10^{6.6}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 10.2 kcal mol^{-1}, and an A factor of $10^{11.7}$ cm^3 mol^{-1} sec^{-1} for CD_3 attack on H_2. This activation energy is probably low since the activation energy (10.6 kcal mol^{-1}) for attack on acetone-d_6 by CD_3 is low by nearly 1 kcal mol^{-1} (*cf.* Table IV). The activation energy for attack on H_2 (10.2 kcal mol^{-1}) is the same as the lower value found by Whittle and Steacie[24] in the same system when using the less accurate method of estimation of methane formed by attack on H_2.

Phibbs and Darwent[81] photolyzed mixtures of H_2 and dimethylmercury, and from their results Whittle and Steacie[24] calculated a rate constant of $10^{6.7}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 9.9 kcal mol^{-1}, and an A factor of $10^{11.7}$ cm^3 mol^{-1} sec^{-1}.

Wijnen and Steacie[82] derived an activation energy for CH_3 attack on H_2 of 10.5 kcal mol^{-1} from the work of Davison and Burton[83] on $CH_3 + D_2$, by assuming a value for the kinetic isotope effect on the activation energy ($E_D - E_H$) of 1.7 kcal mol^{-1}, equal to the zero-point energy difference between H_2 and D_2. That this is not a reliable procedure is clear since several investigations have led to values of ($E_D - E_H$) in the range 0.8–1.1 kcal mol^{-1} with only one value of 1.7 kcal mol^{-1}, from the work of Majury and Steacie,[21,80] shown to be unreliable above. The derived activation energy should be placed in the range 11.1–11.5 kcal mol^{-1} with a corresponding increase in the A factor.

From the photolysis of ketene in the presence of H_2, Gesser and Steacie[84] calculated parameters for the attack of CH_3 on H_2 and reported a rate constant at 164° of $10^{6.4}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 10.2 kcal mol^{-1}, and an A factor of $10^{11.5}$ cm^3 mol^{-1} sec^{-1}.

2. *Attack on D_2*

Of the several investigations of the reaction, few can be ruled out. The range of rate constants at 164° is $10^{5.6}$–$10^{6.0}$ cm^3 mol^{-1} sec^{-1}. Activation energies lie between 10.9 and 13.7 kcal mol^{-1}, with most values near 12.0 kcal mol^{-1}; A factors lie in the range $10^{11.4}$–$10^{12.8}$ cm^3 mol^{-1} sec^{-1}.

Majury and Steacie[21,80] photolyzed mixtures of acetone-d_6 and D_2 and found a rate constant at 164° of $10^{5.9}$ cm^3 mol^{-1} sec^{-1} and an activation energy of 10.9 kcal mol^{-1}. This activation energy may be low since the acetone-d_6 gave a low activation energy (10.6 kcal mol^{-1}) for CD_3 attack on itself. In the photolysis of acetone and D_2 mixtures they[21,80] obtained a rate constant of $10^{5.9}$ cm^3 mol^{-1} sec^{-1} and an activation energy of 11.7 kcal mol^{-1}. These latter values are in very good agreement with Whittle and Steacie's[24] results in the same system where the rate constant at 164° was $10^{5.9}$ cm^3 mol^{-1} sec^{-1} and the activation energy was 11.8 kcal mol^{-1}.

Davison and Burton[83] photolyzed acetone and acetaldehyde in the presence of D_2, and their results and conclusions have been examined by Wijnen and Steacie.[82] In the work with acetone, a rate constant at 164° of $10^{5.6}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 12.2 kcal mol^{-1}, and an A factor of $10^{11.7}$ cm^3 mol^{-1} sec^{-1} were reported.[82] In the work using acetaldehyde as the radical source, the rate constant at 164° reported[82] is $10^{6.0}$ cm^3 mol^{-1} sec^{-1}, in good agreement with other values, but the activation energy, 13.7 kcal mol^{-1}, and the A factor, $10^{12.8}$ cm^3 mol^{-1} sec^{-1}, are much larger than other values.

Chanmugam and Burton[84] photolyzed acetone in the presence of D_2 and report a rate constant for attack on D_2 of $10^{5.7}$ cm^3 mol^{-1} sec^{-1} at 164° with an activation energy of 12.1 kcal mol^{-1} and an A factor of $10^{11.5}$ cm^3 mol^{-1} sec^{-1}. A different investigation[85] of the same system gave a rate constant at 164° of $10^{5.6}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 11.9 kcal mol^{-1}, and an A factor of $10^{11.5}$ cm^3 mol^{-1} sec^{-1}. This work[85] indicated that earlier workers[24,83] had obtained practically identical relative rates of reaction of CH_3 radicals with acetone and D_2 (Figure 1 of ref 85).

Rebbert and Steacie[86] photolyzed dimethylmercury with D_2 and found an activation energy of 12.7 kcal mol^{-1}, a rate constant at 164° of $10^{5.9}$ cm^3 mol^{-1} sec^{-1}, and an A factor of $10^{12.3}$ cm^3 mol^{-1} sec^{-1}.

3. *Attack on HD*

The only results for abstraction from HD are those of Whittle and Steacie[24] who photolyzed both acetone and acetone-d_6 in the presence of HD. In the case of CH_3 radical attack, the rate constant at 164° for H abstraction was $10^{6.1}$ cm^3 mol^{-1} sec^{-1}, a value similar to those for H abstraction from H_2. The activation energy was 10.0 kcal mol^{-1} and the A factor was $10^{11.1}$ cm^3 mol^{-1} sec^{-1}; these figures are low compared with those for H abstraction from H_2.

In the case of D abstraction from HD by CH_3 radicals, two sets of parameters are available from two sets of experiments performed on two mixtures with different relative concentrations of acetone and HD. In the mixture relatively rich in acetone compared with HD, reliable parameters for abstraction of H atoms from HD could not be obtained since the amount of methane formed from attack on HD was small compared with the amount of methane coming from attack on the acetone. The second mixture, relatively rich in HD, yielded the parameters for H abstraction mentioned above.

The two sets of parameters for D abstraction are apparently not identical although the rate constants at 164° are equal ($10^{5.8}$ cm^3 mol^{-1} sec^{-1}). However, as the activation energies differ by only 0.2 kcal mol^{-1} and the A factors are different by a factor of 1.6, the discrepancies could be due to experimental errors.

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(80) T. G. Majury and E. W. R. Steacie, *Discuss. Faraday Soc.*, **14**, 45 (1953).

(81) M. K. Phibbs and B. de B. Darwent, *Trans. Faraday Soc.*, **45**, 541 (1949).

(82) M. H. J. Wijnen and E. W. R. Steacie, *Discuss. Faraday Soc.*, **14**, 118 (1953).

(83) S. Davison and M. Burton, *J. Amer. Chem. Soc.*, **74**, 2307 (1952).

(84) J. Chanmugam and M. Burton, *ibid.*, **78**, 509 (1956).

(85) J. R. McNesby, A. S. Gordon, and S. R. Smith, *ibid.*, **78**, 1287 (1956).

(86) R. E. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **32**, 113 (1954).

Table II

Abstraction of Hydrogen and Deuterium Atoms by Trifluoromethyl Radicals from H_2, HD, and D_2

Substrate	*Radical source*[a]	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k*[b] *(cm^3 mol^{-1} sec^{-1})*		*Ref*
					Overall	*Per atom*	
H_2	HFA	59–158	11.86	9.5	7.1	6.8	88
H_2	HFAzo	219–346	11.59	8.8	7.2	6.9	19
H_2	HFA	60–597	12.14	10.66	6.81	6.51	87
H-D	HFA	102–174	11.78	10.5	6.5	6.5	88
H-D	HFA	60–597	11.94	10.77	6.45	6.45	87
H-*D*	HFA	102–174	11.4	10.2	6.3	6.3	88
H-*D*	HFA	60–597	12.17	11.63	6.35	6.35	87
D_2	HFA	86–196	11.45	10.2	6.4	6.1	88
D_2	HFAzo	219–346	11.44	9.7	6.6	6.3	19
D_2	HFA	60–597	12.01	11.66	6.18	5.88	87

[a] HFA = hexafluoroacetone; HFAzo = hexafluoroazomethane. [b] At 164°.

In the photolysis of acetone-d_6 with HD, only one set of experiments was performed. For H abstraction, the rate constant at 164°, $10^{6.0}$ cm^3 mol^{-1} sec^{-1}, is comparable with those for H abstraction from H_2, but the activation energy, 10.7 kcal mol^{-1}, is higher than most values for attack on H_2. Abstraction of D from HD by CD_3 radicals yields a rate constant at 164° of $10^{5.8}$ cm^3 mol^{-1} sec^{-1}, a value slightly larger than for D abstraction from D_2. The activation energy, 10.7 kcal mol^{-1}, is the same as for H abstraction from HD, the reason for the differing rate constants lying in the different *A* factors.

4. *Kinetic Isotope Effects for Abstraction from H_2, HD, and D_2*

The simple theory of kinetic isotope effects considered in section XI is valid for transition states [R-H-X] in which the masses of R and X are much greater than the mass of the H or D atom being transferred; the moments of inertia of the transition state should not differ significantly whether the atom being transferred is H or D. Neither should substitution of CD_3 radicals for CH_3 have much effect, and no experimental difference has been found between these radicals in their reactions with hydrocarbons (section V). The difference in activation energy for abstraction of H or D atoms from a substrate HX or DX reflects the difference in zero-point energies between the HX and DX bonds.

When HX and DX represent H_2, HD, or D_2, the simplifications above cannot be made since X is no longer massive compared with the atom being transferred. The moments of inertia of CH_3-H-H and CH_3-D-D are different; substitution of CD_3 for CH_3 will change the moment of inertia, although this might be expected to be a small effect compared with the change from H_2 to D_2. Since the difference in zero-point energies of H_2 and D_2 is 1.8 kcal mol^{-1}, activation energy differences for CH_3 attack on H_2 and D_2 might be expected to be the same, 1.8 kcal mol^{-1}, leading to a difference in rate constants (k_H/k_D) at 164° of a factor of 8.3.

For attack on HD, irrespective of whether H or D is removed, an intermediate activation energy is expected; calculation[24] of the difference in moments of inertia of the transition states [CH_3-H-D] and [CH_3-D-H] suggests that abstraction of H should be 1.5 times faster than abstraction of D. Rate constants are thus expected to be different for CH_3 and CD_3 attack on H_2, HD, and D_2 and for both radicals A_H/A_D should differ from unity.

Experimentally, some of these expectations are achieved. In attack on H_2, the ratio of rate constants[21,80] k_{CH_3}/k_{CD_3} is 0.81, and for attack on D_2, k_{CH_3}/k_{CD_3} is 0.68 at 164°. For abstraction of H from HD[24] k_{CH_3}/k_{CD_3} is 0.78, at 164°. Thus the two radicals react at different rates, as expected. The effect is not revealed in higher *A* factors for CD_3 attack because experimental errors are too large to see it.

Experimental isotope effects are listed in Table XXXIX for H_2, HD, and D_2. For H_2 and D_2, the ratio of rate constants k_H/k_D at 164° lies between 3.7 and 4.5, while the difference in activation energies ($E_D - E_H$) is in the range 0.7 to 1.7 kcal mol^{-1} with the latter value[21,24,80] probably too large for experimental reasons. The activation energy difference and the ratio of rate constants are less than expected. In attack on HD the ratio of rate constants at 164° is in the range 1.6–2.0, in good agreement with the expected ratio of 1.5. In only one investigation (CD_3 + HD) is the activation energy difference equal to zero while in the other two, values of 1.1 and 1.3 kcal mol^{-1} are listed.

The work on HD is somewhat ambiguous and its reactions could very profitably be reinvestigated. Indeed, a comprehensive reinvestigation of all three isotopic species would be well worthwhile both from an experimental and from a theoretical viewpoint.

B. ATTACK BY TRIFLUOROMETHYL RADICALS

The available data are listed in Table II. Of the three investigations of CF_3 attack on H_2, HD, or D_2 so far reported, one[87] is recent but the other two were published in 1956.

1. *Attack on H_2*

Ayscough and Polanyi[88] photolyzed hexafluoroacetone in the presence of H_2 and found a rate constant at 164° of $10^{7.1}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 9.5 ± 0.7 kcal mol^{-1}, and an *A* factor of $10^{11.9}$ cm^3 mol^{-1} sec^{-1}. The second investigation used[19] the photolysis of hexafluoroazomethane as the radical source, and with H_2 a rate constant for CF_3 attack of $10^{7.2}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 8.8 kcal mol^{-1}, and an *A* factor of $10^{11.6}$ cm^3 mol^{-1} sec^{-1} were obtained. Thus, the two early determinations are in rough agreement in activation energy, and the rate constants are practically identical.

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(87) C. L. Kibby and R. E. Weston, *J. Chem. Phys.*, **49**, 4825 (1968).

(88) P. B. Ayscough and J. C. Polanyi, *Trans. Faraday Soc.*, **52**, 960 (1956).

The most recent investigation also used[87] hexafluoroacetone photolysis as the radical source. In the photolysis with H_2, a rate constant at 164° of $10^{6.8}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 10.7 kcal mol^{-1}, and an A factor of $10^{12.1}$ cm^3 mol^{-1} sec^{-1} were obtained. These figures are preferred to the two earlier determinations.

2. *Attack on D_2*

All three groups of investigators have studied the reaction of CF_3 radicals with D_2, and their results are not in good agreement. The first investigators found[88] a rate constant at 164° of $10^{6.4}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 10.2 ± 0.7 kcal mol^{-1}, and an A factor of $10^{11.4}$ cm^3 mol^{-1} sec^{-1}, while the second[19] found a rate constant at 164° of $10^{6.6}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 9.7 kcal mol^{-1}, and an A factor of $10^{11.4}$ cm^3 mol^{-1} sec^{-1}. In view of the experimental errors, the A factors and activation energies are not significantly different. The most recent results[87] are markedly different, however. The rate constant at 164°, $10^{6.2}$ cm^3 mol^{-1} sec^{-1}, is lower than the others[19,88] by factors of 1.6 and 2.5, respectively. The activation energy, 11.7 kcal mol^{-1}, is larger by 1.5 kcal mol^{-1} than the highest value previously reported, and the A factor, $10^{12.0}$ cm^3 mol^{-1} sec^{-1}, is larger by a factor of 4. The most recent work seems the most reliable.

3. *Attack on HD*

Only two investigations[87,88] have been made of CF_3 attack on the HD molecule. The earlier of the two, using hexafluoroacetone as the radical source,[88] yielded a rate constant for H abstraction of $10^{6.5}$ cm^3 mol^{-1} sec^{-1} at 164°, an activation energy of 10.5 ± 1.5 kcal mol^{-1}, and an A factor of $10^{11.8}$ cm^3 mol^{-1} sec^{-1}. Compared with their work on H_2, the activation energies are the same for abstraction of H from H_2 and HD within very wide error limits, while the A factors are the same. The rate constants at 164° differ by a factor of 2.

For the abstraction of D from HD, a rate constant at 164° of $10^{6.3}$ cm^3 mol^{-1} sec^{-1} was obtained, the activation energy was 10.2 ± 1.5 kcal mol^{-1}, and the A factor was $10^{11.4}$ cm^3 mol^{-1} sec^{-1}. It is evident that errors associated with the activation energies for abstraction from H_2, HD, or D_2 render pointless the evaluation of differences in activation energy arising from isotopic substitution. At 164°, the ratios of rate constants for attack on H_2 and D_2 can be written as $k_{H_2}/k_{D_2} = 5.0$, while for attack on HD, k_H/k_D is 1.6.

The recent investigation[87] of CF_3 attack on HD yields rate constants and Arrhenius parameters with smaller errors than the earlier work. For H abstraction, the rate constant at 164° ($10^{6.66}$ cm^3 mol^{-1} sec^{-1}) is slightly larger than that from the earlier work[88] on HD ($10^{6.5}$ cm^3 mol^{-1} sec^{-1}) and that from the same work[87] for H abstraction from H_2 ($10^{6.51}$ cm^3 mol^{-1} sec^{-1} on a per atom basis). The activation energy, 10.77 kcal mol^{-1}, is not significantly different from the activation energy[87] for abstraction of H from H_2 (10.66 kcal mol^{-1}). Also, the A factors are very similar at $10^{12.0}$ and $10^{12.1}$ cm^3 mol^{-1} sec^{-1} for attack on HD and H_2, respectively.

For abstraction of D from HD, the rate constant at 164° ($10^{6.3}$ cm^3 mol^{-1} sec^{-1}) is greater than that for D abstraction from D_2 by a factor of 3 when the results for D_2 are expressed on a per atom basis. This is a result of a difference in A factors since the activation energies are identical.

At 164°, the isotope effect for abstraction from HD can be expressed as $k_H/k_D = 1.3$, $E_D - E_H = 0.86$ kcal mol^{-1}, and $A_H/A_D = 0.78$. The equivalent isotope effect for abstraction of H or D from H_2 or D_2, obtained by comparing the separate experimental results, can be expressed as $k_H/k_D = 4.3$, $E_D - E_H = 1.05$ kcal mol^{-1}, and $A_H/A_D = 1.35$. It is significant that the equivalent ratios of rate constants from the earlier work,[88] 1.6 (for HD) and 5.0 (for H_2 and D_2), are in general agreement.

The theory of isotope effects, given in section XI and presented in a modified form in section IV.A.4 above predicts that the ratio of rate constants, k_H/k_D, should be less for attack on HD than for attack on H_2 and D_2. This is found experimentally. At 164°, k_H/k_D is in the range 1.3–1.6 for CF_3 attack on HD and in the range 4.0–5.0 for attack on H_2 and D_2. The theory suggests that there should be no activation energy difference for abstraction of H or D from HD, but the recent results[87] indicate a difference of 0.86 ± 0.20 kcal mol^{-1}. An Arrhenius plot of the rate constants for overall abstraction from H_2, HD, and D_2 (taking the sum $k_H + k_D$ for attack on HD) indicates[87] that the activation energy for attack on HD lies between those for attack on H_2 and D_2, in accord with expectations based on the intermediate bond dissociation energy in HD. However, two aspects of the recent work cast doubts on the application of the simple theory. The first is the activation energy difference of 0.86 ± 0.20 kcal mol^{-1} for attack at H and D, mentioned above. The second is that, over the unusually large temperature range (60–597°) used, nonlinear Arrhenius plots were obtained. Values of k_H/k_D varied from 1.6 to 2.5 between the extremes of the temperature range.

V. Abstraction from CH and CD Bonds

As might be expected this section is the longest and most of the data refer to attack by methyl radicals. The subjects have been subdivided by considering attack on the groups CH_3, CH_2, and CH (and their deuterated derivatives) in different molecular environments.

A. ATTACK BY METHYL RADICALS

1. *On CH_3 and CD_3 Groups*

Kinetic data for the attack by methyl (CH_3 or CD_3) radicals on CH_3 and CD_3 groups are presented in Tables III and IV, respectively.

The particular molecular environment of a CH_2 group has a great effect on its reactivity toward attack by methyl radicals. At the two extremes, the reactivity of CH_2 in 1,2-dimethylhydrazine[89] is some 2500 times that in methane[90,91] (on a per CH_2 group basis, at 164°). Within a particular class of compounds, methyl group reactivities remain much more constant.

The rates of attack on the methyl groups in the saturated hydrocarbons (methane,[90,91] ethane,[90,92] propane, *n*-butane, isobutane,[90] neopentane,[92–94] and hexamethylene[92]) lie

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Table III

Methyl Radical Attack on Methyl Groups

CH_3 (or CD_3) + $X\mathit{CH}_3 \longrightarrow CH_3H$ (or CD_3H) + XCH_2

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k^a (cm^3 mol^{-1} sec^{-1})*		*Ref*
					Overall	*Per CH_3 group*	
$H\mathit{CH}_3$	Acetone-d_6	350–428	11.76	14.23	4.65	4.52	90
$H^{14}\mathit{CH}_3$	Acetone	200–350	11.83	14.65	4.50	4.38	91
$CH_3\mathit{CH}_3$	Acetone-d_6	116–394	11.1	10.4	5.9	5.6	92
$CH_3\mathit{CH}_3$	Acetone-d_6	260–490	12.17	11.73	6.30	6.00	90
$CD_3\mathit{CH}_3$	Acetone-d_6	270–464	11.83	11.83	5.96	5.96	90
$CH_3CD_2\mathit{CH}_3$	Acetone-d_6	296–420	12.04	11.53	6.27	5.97	90
$CH_3(CH_2)_2CH_3$	Acetone-d_6	356–450	12.05	11.63	6.23	5.93	90
$(CH_3)_2CD\mathit{CH}_3$	Acetone-d_6	295–456	12.18	11.53	6.41	5.93	90
$(CH_3)_3C\mathit{CH}_3$	Acetone	138–292	11.3	10.0	6.3	5.7	92
$(CH_3)_3C\mathit{CH}_3$	$HgMe_2$	131–251	11.2	10.4	6.1	5.5	93
$(CH_3)_3C\mathit{CH}_3$	Acetone-d_6	185–309	12.33	12.01	6.32	5.70	94
$((CH_3)_3C)_2$	Acetone-d_6	25–340	11.2	9.5	6.4	5.6	92
$(CH_3)\ C{=}C(CH_3)_2$	Biacetyl	80–130	11.11	8.9	6.66	6.06	36
$C_6H_5\mathit{CH}_3$	Acetone	107–300	11.6	9.5	6.8	6.8	95
$(CH_3)_3Si\mathit{CH}_3$	Azomethane	50–200	11.5	10.3	6.4	5.8	96
$ND_2\mathit{CH}_3$	Azomethane	115–175	11.15	9.00	6.65	6.65	25
$NH_2\mathit{CH}_3$	Azomethane	115–175	11.0	8.7	6.6	6.6	25
$CH_3ND\mathit{CH}_3$	Azomethane	120–175	11.46	8.70	7.11	6.81	97
$ND_2N(\mathit{CH}_3)_2$	Azomethane	112–175	~11.0	~7.2	7.4	7.1	89
$(CH_3)_2N\mathit{CH}_3$	Acetone-d_6	193–302	11.8	8.8	7.4	6.9	98
$(CH_3)_2N\mathit{CH}_3$	Acetone	132–269	11.4	8.0	7.4	6.9	99
$(CH_3)_2N\mathit{CH}_3$	Acetone	123–232	11.9	8.9	7.4	6.9	100
CH_3NNCH_3	Azomethane	90–175	10.93	7.84	7.01	6.71	25
CH_3NNCH_3	Azomethane	110–175	10.85	7.83	6.93	6.63	101
$NH_2CH_2\mathit{CH}_3$	Azomethane	110–180	...	...	~5.8	~5.8	97
$CH_3(ND)_2\mathit{CH}_3$	Azomethane	80–180	~11.6	~6.6	~8.3	~8.0	89
$DO\mathit{CH}_3$	Acetone-d_6	140–250	11.29	10.05	6.26	6.26	66
$HO\mathit{CH}_3$	Acetone	154–204	11.4	10.40	6.2	6.2	102
$HO\mathit{CH}_3$	Acetone	125–245	10.4	8.14	6.3	6.3	103
$HOCH_2\mathit{CH}_3$	Acetone	130–250	...	...	~5.6	~5.6	112
$CH_3O\mathit{CH}_3$	$HgMe_2$	100–250	10.8	8.4	6.6	6.3	104
$CH_3O\mathit{CH}_3$	Acetone	108–198	11.3	9.5	6.5	6.2	98
$CH_3O\mathit{CH}_3$	Hg photosensitized decompn	25–292	11.6	10.0	6.6	6.3	105
$CH_3O\mathit{CH}_3$	Hg photosensitized decompn	200–300	11.06	9.4	6.4	6.1	106
$CH_3O\mathit{CH}_3$	Acetone	135–250	11.6	10.0	6.6	6.3	66
$NH_2O\mathit{CH}_3$	Azomethane	70–190	...	...	~6.7	~6.7	107
$CH_3OO\mathit{CH}_3$	Dimethyl peroxide	124–185	12.56	10.0	7.6	7.3	108
$HCOO\mathit{CH}_3$	Acetone	120–240	10.01	8.95	5.55	5.55	109
$CD_3COO\mathit{CH}_3$	Acetone	140–300	11.23	11.86	5.30	5.30	110
$CH_3CO\mathit{CH}_3$	Acetone	129–248	11.46	9.64	6.64	6.34	112
$CH_3CO\mathit{CH}_3$	Acetone	122–253	11.35	9.53	6.58	6.28	113
$CH_3CO\mathit{CH}_3$	Acetone	100–300	11.52	9.72	6.66	6.36	23
$CH_2CO\mathit{CH}_3$	Acetone	113–300	11.53	9.87	6.59	6.29	114
$(CH_3CO)_2$	Biacetyl	404–503	11.8	9.1	7.2	6.9	115
CH_3COOCD_3	Acetone	151–274	11.1	10	6.1	6.1	116
CH_3COOCD_3	Acetone	120–300	11.27	9.85	6.34	6.34	110
$NH_2CO\mathit{CH}_3$	Acetone-d_6	122–259	11.00	10.33	5.83	5.83	68
$NH_2CO\mathit{CH}_3$	Acetone	143–224	10.7	9.2	6.1	6.1	117
$DOOC\mathit{CH}_3$	Acetic acid	105–285	11.1	10.2	6.0	6.0	119
CH_3CDO	Azomethane	27–165	10.9	7.8	7.0	7.0	118
$F\mathit{CH}_3$	Acetone-d_6	193–331	11.2	11.8	5.3	5.3	111

[a] At 164°

remarkably close to one another. With the exception of methane, which is relatively inert toward attack by methyl radicals, at 164° and on a per CH_3 group basis, the rates of abstraction differ only by a factor of about 3, from k (cm^3 mol^{-1} sec^{-1}) = $10^{5.5}$ or $10^{5.7}$ (for neopentane) to $10^{5.97}$ (for propane). The A factors for these reactions show no particular trend and lie in the range $10^{11.1}$–$10^{12.3}$ cm^3 mol^{-1} sec^{-1}. The origin of the inertness of methane toward methyl attack lies in the large

Table IV

Methyl Radical Attack on Methyl-d_3 Groups

CH_3 (or CD_3) + $XCD_3 \longrightarrow CH_3D$ (or CD_4) + XCD_2

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log K^a (cm³ mol⁻¹ sec⁻¹)* Overall	*Per CD_3 group*	*Re*
$\mathrm{D}\mathit{CD}_3$	Acetone	153–428	11.25	12.93	4.78	4.66	120
$\mathrm{D}^{14}\mathit{CD}_3$	Acetone-d_6	200–350	12.61	17.8	3.71	3.59	121
$\mathrm{CD_3}\mathit{CD}_3$	Acetone-d_6	260–490	12.17	13.23	5.55	5.25	90
$\mathrm{CH_3}\mathit{CD}_3$	Acetone-d_6	270–464	12.03	13.73	5.16	5.16	90
$\mathrm{C_6H_5}\mathit{CD}_3$	Acetone	100–300	11.6	11.3	5.9	5.9	95
$\mathrm{NH_2}\mathit{CD}_3$	Azomethane	125–175	10.86	10.10	5.81	5.81	25
$\mathrm{HO}\mathit{CD}_3$	Acetone	135–250	11.34	11.93	5.37	5.37	66
$\mathrm{HO}\mathit{CD}_3$	Acetone	154–204	11.25	11.70	5.40	5.40	102
$\mathrm{HO}\mathit{CD}_3$	Acetone-d_6	125–245	10.2	9.3	5.5	5.5	103
$\mathrm{CH_3COO}\mathit{CD}_3$	Acetone	120–300	11.47	12.05	5.44	5.44	110
$\mathrm{CD_3CO}\mathit{CD}_3$	Acetone-d_6	130–250	11.62	11.54	5.85	5.55	112
$\mathrm{CD_3CO}\mathit{CD}_3$	Acetone-d_6	130–220	11.57	11.29	5.92	5.62	69
$\mathrm{CD_3CO}\mathit{CD}_3$	Acetone-d_6	80–250	11.66	11.44	5.94	5.64	103
$\mathrm{CD_3CO}\mathit{CD}_3$	Acetone-d_6	200–350	11.74	11.42	6.03	5.73	121
$\mathrm{NH_2CO}\mathit{CD}_3$	Acetone-d_6	122–259	11.15	11.47	5.41	5.41	68
$\mathit{CD}_3\mathrm{COOCH_3}$	Acetone	140–300	11.61	15.45	3.88	3.88	110
$\mathit{CD}_3\mathrm{SH}$	Acetone	127–203	10.9	8.3	6.7	6.7	69

^{a} At 164°

activation energy (E = 14.2 or 14.6 kcal mol^{-1}). The activation energies for abstraction from the other six hydrocarbons are all significantly lower and lie between 10.0 and 12.0 kcal mol^{-1}.

These results are in general accord with expectations based on differences in bond dissociation energies (see Appendix II). The values (kcal mol^{-1}) of 99.3 ± 1, 98 ± 2, and 98 ± 1 for $D((CH_3)_3CCH_2\text{–}H)$, $D(CH_3CH_2CH_2\text{–}H)$, and $D(CH_3CH_2\text{–}H)$ are similar to one another but markedly lower than the value of $D(CH_3\text{–}H)$ for methane of 104 ± 1 kcal mol^{-1}.

The reactivity of a methyl group attached to a carbon-carbon double bond[36] (in tetramethylethylene) is only marginally greater than that of a methyl group attached to saturated carbon. At 164°, on a per CH_3 basis, k is $10^{6.1}$ cm³ mol^{-1} sec^{-1} compared with the average value for saturated hydrocarbons of $10^{5.8}$ cm³ mol^{-1} sec^{-1}.

The enhanced reactivity of the CH_3 group in toluene[95] (at 164°, k is $10^{6.8}$ cm³ mol^{-1} sec^{-1}) indicates an activating effect by the phenyl group. This behavior is in accord with the lower bond dissociation energy, $D(C_6H_5CH_2\text{–}H)$ = 85 ± 1 kcal mol^{-1}, though on this basis an activation energy lower than the experimentally observed value of 9.5 kcal mol^{-1} might be expected.

It is relevant to note here that in tetramethylsilane[96] the rate parameters for abstraction of hydrogen (at 164°, $k = 10^{6.4}$ cm³ mol^{-1} sec^{-1}, $A = 10^{11.5}$ cm³ mol^{-1} sec^{-1}, and E = 10.3 kcal mol^{-1}) are close to the values obtained for neopentane ($k = 10^{6.3}$ or $10^{6.1}$ cm³ mol^{-1} sec^{-1}, $A = 10^{11.3}$ or $10^{11.2}$ cm³ mol^{-1} sec^{-1}, and E = 10.0 or 10.4 kcal mol^{-1}). This indicates that the central atoms, carbon and silicon, have similar activating effects on the attached methyl groups.

The rate constants for abstraction from methyl groups attached to a nitrogen atom are markedly greater than for abstraction from methyl groups attached to carbon in saturated hydrocarbons. At 164°, on a per CH_3 group basis, the average rate constant for abstraction from methylamine,[25] dimethylamine,[97] trimethylamine,[98–100] and 1,1-dimethylhydrazine[89] (omitting the value for 1,2-dimethylhydrazine[89] which is anomalously high) is $10^{6.9}$ cm³ mol^{-1} sec^{-1}, more than a factor of 10 greater than the average value shown for hydrocarbons. The superior reactivity is wholly accounted for by the lower activation energies (values lie between *ca.* 7.2 and 9.0 kcal mol^{-1}) since the A factors also have lower values than they do for hydrocarbons. This situation almost certainly reflects bond dissociation energies lower than in corresponding hydrocarbons. Like the methyl groups in hydrocarbons, the CH_3 groups in the amines do not differ in reactivity by much—in methylamine, dimethylamine, trimethylamine, and 1,1-dimethylhydrazine, values for k, at 164°, differ only by a factor of 3.

The kinetic results[25,101] for attack on azomethane reveal the reactivity of a methyl group attached to a nitrogen double bond. Somewhat surprisingly, the reactivity is close to that found in saturated amines. At 164°, on a per CH_3 group basis, $k = 10^{6.7}$ cm³ mol^{-1} sec^{-1} which can be compared with the average value for amines of $10^{6.9}$ cm³ mol^{-1} sec^{-1}. The Arrhenius parameters also lie close to those for attack on amines.

The reactivity of methyl groups attached to an oxygen atom (in methanol,[66,102,103] dimethyl ether,[66,98,104–106] O-methyl-

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hydroxylamine,[107] dimethyl peroxide,[108] methyl formate,[109] and methyl acetate[110]) seem to show wide variation. At 164°, on a per CH_3 group basis, rate constants range from k (cm^3 mol^{-1} sec^{-1}) = $10^{5.3}$ (for methyl acetate) to $10^{7.3}$ (for dimethyl peroxide). Both these extreme values, however, are open to doubt; the peroxide results require an anomalously high A factor ($10^{12.5}$ cm^3 mol^{-1} sec^{-1}) and the acetate results show extraordinary isotope effects (see section XI). Both investigations may have suffered from interference by secondary reactions. At 164°, the rate constants (cm^3 mol^{-1} sec^{-1}) on a per CH_3 group basis, for abstraction from methanol ($k = 10^{6.2}$–$10^{6.3}$), dimethyl ether ($k = 10^{6.1}$–$10^{6.3}$), and O-methylhydroxylamine (k = *ca.* $10^{6.7}$) are probably not significantly different from one another. At the same temperature, the rate constant for abstraction from the methyl group in methanol ($k = 10^{6.3}$ cm^3 mol^{-1} sec^{-1}) lies between the values for attack on the methyl groups of the isoelectronic ethane ($k = 10^{5.6}$ or $10^{6.0}$ cm^3 mol^{-1} sec^{-1}) and methylamine ($k = 10^{6.7}$ cm^3 mol^{-1} sec^{-1}). Similarly, at 164°, the reactivity of the methyl groups in dimethyl ether ($k = 10^{6.1}$–$10^{6.3}$ cm^3 mol^{-1} sec^{-1} on a per CH_3 group basis) lies midway between values for propane ($k = 10^{6.0}$ cm^2 mol^{-1} sec^{-1}) and dimethylamine ($k = 10^{6.9}$ cm^3 mol^{-1} sec^{-1}). The rate constant for abstraction from the methyl group of methyl formate, however, is markedly low (k, at 164°, is $10^{5.6}$ cm^3 mol^{-1} sec^{-1}).

At 164°, the rate constant for attack on methanol lies close to that for attack on dimethyl ether and the recommended bond dissociation energies $D(H–CH_2OH) = 92 \pm 2$ and $D(H–CH_2OCH_3) = 92.9$ kcal mol^{-1} are not significantly different. It is thus reasonable to expect the Arrhenius parameters to be similar. The preferred values for attack on methanol (see section VII) are $A = 10^{11.29}$ cm^3 mol^{-1} sec^{-1} and E = 10.1 kcal mol^{-1}. The Arrhenius parameters reported for attack on dimethyl ether are rather scattered (values for A range from $10^{10.8}$ to $10^{11.6}$ cm^3 mol^{-1} sec^{-1}, and values for E range from 8.4 to 10.0 kcal mol^{-1}). By analogy with methanol, the dimethyl ether results giving the parameters $A = 10^{11.6}$ cm^3 mol^{-1} sec^{-1} and E = 10.0 kcal mol^{-1} seem to be most acceptable. The relative inertness of the methyl group in methyl formate is due to an unexpectedly low A factor ($10^{10.0}$ cm^3 mol^{-1} sec^{-1}) since the activation energy is also low (E = 9.0 kcal mol^{-1}).

The kinetic data for abstraction from methyl fluoride[111] constitute the only results available for attack on methyl halides (secondary reactions occurring in the methyl chloride system makes valid reaction rates difficult to measure). Methyl fluoride is relatively inert (at 164°, $k = 10^{5.3}$ cm^3 mol^{-1} sec^{-1}) owing to the high activation energy (E = 11.8 kcal mol^{-1}). These results are in accord with the bond dissociation energy of 101 ± 4 kcal mol^{-1} reported for $D(H–CH_2F)$.

When methyl groups are attached to carbonyl groups (as in acetone,[23,112-114] biacetyl,[115] methyl acetate,[110,116] acetamide,[68,117] acetaldehyde,[118] and acetic acid[119]), the rate constants, at 164° on a per CH_3 group basis, range from $10^{5.83}$ cm^3 mol^{-1} sec^{-1} (in acetamide) to $10^{7.0}$ cm^3 mol^{-1} sec^{-1} (in acetaldehyde). A factors vary from $10^{10.7}$ to $10^{11.8}$ cm^3 mol^{-1} sec^{-1} and activation energies from 9.1 to 10.3 kcal mol^{-1}. The similar rate parameters reported for acetone (typical values are $A = 10^{11.5}$ cm^3 mol^{-1} sec^{-1}, E = 9.7 kcal mol^{-1}) and methanol ($A = 10^{11.8}$ cm^3 mol^{-1} sec^{-1}, E = 10.1 kcal mol^{-1}) are consistent with the known bond dissociation energies of $D(HOCH_2–H)$ and $D(CH_3COCH_2–H)$ both reported as 92 kcal mol^{-1}.

It is important to note that where (as in ethylamine[97] and ethanol[112]) the CH_3 group is not directly linked to an activating atom, the reactivity of the methyl group falls to a value near to that found for hydrocarbons. For methyl groups in ethylamine and ethanol, values for k (164°) of *ca.* $10^{5.8}$ and *ca.* $10^{5.6}$ cm^3 mol^{-1} sec^{-1} are found. These can be compared with the average value for hydrocarbons of $10^{5.8}$ cm^3 mol^{-1} sec^{-1} (see above).

The kinetic data available for abstraction from methyl-d_3 groups (Table IV), although less extensive, show similar features to the data for abstraction from methyl groups.

The reactivity of CD_3 in methane-d_4[120,121] is markedly lower than that in either ethane-d_3 or ethane-d_6.[90] At 164°, on a per CD_3 group basis, the rate constants (cm^3 mol^{-1} sec^{-1}) are $10^{4.7}$ or $10^{3.6}$ (methane-d_4), $10^{5.3}$ (ethane-d_6), and $10^{5.2}$ (ethane-d_3).

The activating effect of the phenyl group is again shown by the enhanced reactivity of CD_3 in toluene-d_3[95] (k, at 164°, is $10^{5.9}$ cm^3 mol^{-1} sec^{-1}).

Like the undeuterated analogs, the reactivity of CD_3 in methanol-d_3[66,102,103] is intermediate between that in the deuterated ethanes and in methylamine-d_3.[25] At 164°, on a per CD_3 group basis, values for k (cm^3 mol^{-1} sec^{-1}) are $10^{5.3}$ (ethane-d_6), $10^{5.2}$ (ethane-d_3), $10^{5.4}$ (methanol-d_3), and $10^{5.8}$ (methylamine-d_3).

The reactivities of CD_3 attached to an oxygen atom in methanol-d_3 and methyl acetate-d_3[110] appear close (the rate constants, at 164°, are $10^{5.37}$ and $10^{5.44}$ cm^3 mol^{-1} sec^{-1}, respectively) though this may be fortuitous in view of the doubts about the methyl acetate results.

The effect on its reactivity of attaching CD_3 to a sulfur atom is shown by the results[69] for attack on methylthiol-d_3. The effect is an enhancement of reactivity: at 164°, $k = 10^{6.7}$ cm^3 mol^{-1} sec^{-1} compared with a value of $10^{5.4}$ cm^3 mol^{-1} sec^{-1} for attack on the CD_3 group in methanol-d_3. The origin lies in the lowering in activation energy to 8.3 kcal mol^{-1} compared with the value of 11.9 kcal mol^{-1} found for methanol-d_3.

The reactivities of methyl-d_3 groups attached to carbonyl groups in acetone-d_6[69,103,112,121] and acetamide-d_3[68] are close. At 164°, on a per CD_3 basis, k (cm^3 mol^{-1} sec^{-1}) is *ca.* $10^{5.6}$ (acetone-d_6) and $10^{5.4}$ (acetamide-d_3). The allegedly low reactivity of the CD_3 group in methyl acetate, CD_3COOCH_3 (at 614°, $k = 10^{3.9}$ cm^3 mol^{-1} sec^{-1}), must be viewed with some doubt.

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Table V

Methyl Radical Attack on Methylene Groups

$\mathrm{CH_3\ (or\ CD_3) + XYCH_2 \longrightarrow CH_3H\ (or\ CD_3H) + XYCH}$

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k^a (cm^3 mol^{-1} sec^{-1})* Overall	*Per CH$_2$ group*	*Ref*
$(\mathrm{CH_3})_2CH_2$	Acetone-d_6	300–452	11.82	10.13	6.75	6.75	90
$\mathrm{CH_3(C_2H_5)}CH_2$	Acetone-d_6	250–450	11.87	9.53	7.10	6.80	90
$(\mathrm{CH_2})_3$	Acetone-d_6	139–292	11.0	10.3	5.8	5.3	98
$(\mathrm{CH_2})_3$	$\mathrm{HgMe_2}$	100–250	11.1	10.2	6.0	5.5	104
$(\mathrm{CH_2})_3$	Acetone-d_6	248–404	11.7	13.1	5.1	4.6	122
$(\mathrm{CH_2})_4$	Acetone-d_6	154–307	11.4	9.3	6.7	6.1	98
$(\mathrm{CH_2})_4$	Acetone-d_6	262–402	12.18	10.1	7.1	6.5	123
$(\mathrm{CH_2})_5$	Acetone-d_6	66–296	11.4	8.3	7.2	6.5	98
$(\mathrm{CH_2})_5$	Acetone-d_6	250–402	12.24	9.1	7.6	6.9	122
$(\mathrm{CH_2})_5$	Acetone-d_6	160–500	12.0	9.3	7.3	6.6	124
$(\mathrm{CH_2})_6$	Acetone	65–189	11.3	8.3	7.1	6.3	98
$(\mathrm{CH_2})_6$	$\mathrm{HgMe_2}$	81–220	11.2	8.3	7.0	6.2	93
$(\mathrm{CH_2})_6$	Acetone-d_6	254–481	12.0	9.8	7.1	6.3	125
$(\mathrm{CH_2})_7$	Acetone-d_6	254–481	12.0	9.2	7.4	6.6	125
$\mathrm{H}CH_2\mathrm{NH_2}$	Azomethane	115–175	11.15	9.00	6.65	6.47	25
$\mathrm{H}CH_2\mathrm{ND_2}$	Azomethane	115–175	11.0	8.7	6.6	6.4	25
$\mathrm{CH_3}CH_2\mathrm{NH_2}$	Azomethane	110–180	11.17	8.12	7.11	7.11	126
$\overline{CH_2\mathrm{CH_2ND}}$	Azomethane	110–175	11.4	10.1	6.3	6.0	101, 127
$\mathrm{ND_2}CH_2\mathrm{CH_2ND_2}$	Azomethane	90–175	10.93	7.31	7.27	6.97	78
$\mathrm{H}CH_2\mathrm{OD}$	Acetone-d_6	140–250	11.29	10.05	6.26	6.08	66
$\mathrm{H}CH_2\mathrm{OH}$	Acetone	154–204	11.4	10.40	6.2	6.0	102
$\mathrm{H}CH_2\mathrm{OH}$	Acetone	125–245	10.4	8.14	6.3	6.1	103
$\mathrm{CH_3}CH_2\mathrm{OH}$	Acetone	130–250	11.60	9.69	6.75	6.75	112
$\overline{CH_2\mathrm{CH_2O}}$	$\mathrm{HgMe_2}$	100–200	11.0	9.6	6.2	5.9	104
$\overline{CH_2\mathrm{CH_2O}}$	$\mathrm{HgMe_2}$	100–250	10.4	9.0	5.9	5.6	128
$\mathrm{CH_2O}$	Di-*tert*-butyl peroxide	122–147	11.25	6.60	8.95	8.95	129
$\mathrm{CH_2O}$	Azomethane	80–180	12.56	6.20	9.46	9.46	130
$\mathrm{F}CH_2\mathrm{F}$	Acetone-d_6	122–301	11.0	10.4	5.8	5.8	111

[a] At 164°.

Table VI

Methyl Radical Attack on Methylene-d_2 Groups

$\mathrm{CH_3\ (or\ CD_3) + XYCD_2 \longrightarrow CH_3D\ (or\ CD_4) + XYCD}$

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k^a (cm^3 mol^{-1} sec^{-1})* Overall	*Per CD$_2$ group*	*Ref*
$(\mathrm{CH_3})_2CD_2$	Acetone-d_6	296–420	11.81	11.53	6.04	6.04	90
$\mathrm{CH_3(CH_3CD_2)}CD_2$	Acetone-d_6	356–450	12.08	11.6	6.26	5.96	90
$\mathrm{D}CD_2\mathrm{OH}$	Acetone	135–250	11.34	11.93	5.37	5.37	66
$\mathrm{D}CD_2\mathrm{OH}$	Acetone	154–204	11.25	11.70	5.40	5.40	102
$\mathrm{D}CD_2\mathrm{OH}$	Acetone-d_6	125–245	10.2	9.3	5.5	5.5	103
$\mathrm{CH_3}CD_2\mathrm{OH}$	Acetone	130–250	11.61	11.40	5.91	5.91	112
$\mathrm{D_2CO}$	Azomethane	80–180	12.65	7.90	8.70	8.40	130

[a] At 164°.

2. On CH$_2$ and CD$_2$ Groups

Tables V and VI present data for the attack of methyl radicals on methylene and methylene-d_2 groups, respectively. In these tables some data for attack on $\mathrm{CH_3}$ and $\mathrm{CD_3}$ groups have been included for comparison.

At 164°, on a per $\mathrm{CH_2}$ group basis, the rate constants for attack on the methylene groups in propane and *n*-butane[90] are close to one another; $k = 10^{6.75}$ cm^3 mol^{-1} sec^{-1} (propane) and $10^{6.80}$ cm^3 mol^{-1} sec^{-1} (*n*-butane). This behavior is in accord with the bond dissociation energies, $D((\mathrm{CH_3})_2\mathrm{CH{-}H})$ being 94.5 ± 1 and $D(\mathrm{CH_3CH_2CH(CH_3){-}H})$ being 94.6 ± 1 kcal mol^{-1}. The larger overall rate constant, at 164°, for attack on *n*-butane has its origin in a smaller activation energy (E = 10.1 kcal mol^{-1} (propane) and 9.5 kcal mol^{-1} (butane)) since the *A* factors are similar. On the basis of bond energy considerations one would expect the origin to lie in a greater *A* factor; however, it is possible that the experimental errors are such that the differences between the Arrhenius parameters are not significant.

The lack of agreement between different investigators using the same cyclic hydrocarbons makes the accurate evaluation of changes impossible. However, it can be seen that cyclopropane[98,104,122] is the least reactive member of the series (at 164° and on a per CH_2 group basis, $k = 10^{4.6}$–$10^{5.3}$ cm^3 mol^{-1} sec^{-1}) and that this is due to the fact that abstraction from it has the largest activation energy. Reactivity increases as the rings get larger, and there appears little significant difference in reactivity between cyclobutane,[98,123] cyclopentane,[98,122,124] cyclohexane,[93,98,125] and cycloheptane.[125] (At 164°, on a per CH_2 basis, *k*'s lie between $10^{6.1}$ and $10^{6.9}$ cm^3 mol^{-1} sec^{-1}.) This trend is reflected by the bond dissociation energies. In kcal mol^{-1}, these are $D(C_3H_5–H) = 101 \pm 3$, $D(C_4H_7–H) = 95 \pm 3$, $D(C_5H_9–H) = 93 \pm 3$, $D(C_6H_{11}–H) = 94 \pm 3$, and $D(C_7H_{13}–H) = 93 \pm 3$.

When methylene groups are situated next to nitrogen atoms in amines and amine-like compounds, their reactivities toward methyl radical attack are enhanced. Comparison of the results for ethylamine[126] and propane[90] shows that, at 164°, the reactivity of the CH_2 group in ethylamine is some 25 times greater than in propane. Similarly, at 164°, and on a per CH_2 group basis, the reactivity of CH_2 in ethylenimine[101,127] is some eight times that in cyclopropane, and in $ND_2CH_2CH_2ND_2$[78] the CH_2 reactivity is about 1.5 times that in *n*-butane.

A comparison of the experimental data for methylamine and ethylamine shows that, at 164°, substitution of CH_3 for H in $H–CH_2NH_2$ increases the reactivity of the methylene group from $k = 10^{6.5}$ cm^3 mol^{-1} sec^{-1} (methylamine) to $k = 10^{7.1}$ cm^3 mol^{-1} sec^{-1} (ethylamine). These increases in reactivity, brought about when CH_2 groups are situated next to nitrogen atoms, are caused by activation energy decreases since the *A* factors are either not significantly different or are smaller for the more reactive species.

Data for the reactivity of methylene groups attached to oxygen atoms are presented in Table V for ethanol,[112] ethylene oxide,[104,128] and formaldehyde.[129,130] Ethanol, propane, and ethylamine form an isoelectronic series, and a consideration of the reactivities at 164° shows that the CH_2 group is most reactive in ethylamine ($k = 10^{7.1}$ cm^3 mol^{-1} sec^{-1}). In propane and ethanol the rate constants, at 164°, for attack on the CH_2 group are both $10^{6.8}$ cm^3 mol^{-1} sec^{-1} (*cf.* the series ethane, methylamine, and methanol above). The reactivity of the CH_2 in ethylenimine is greater than that of the isoelectronic cyclopropane and ethylene oxide. At 164°, and on a per CH_2 group basis, *k* (cm^3 mol^{-1} sec^{-1}) is $10^{3.6}$ or $10^{5.9}$ (ethylene oxide), $10^{4.6}$–$10^{5.3}$ (cyclopropane), and $10^{6.0}$ (ethylenimine).

A comparison of the CH_2 group reactivities in methanol and ethanol shows the activating effect of a methyl group. Substituting CH_3 for H in methanol causes an increase in the rate of attack at the CH_2 group from $10^{6.1}$ to $10^{6.8}$ cm^3 mol^{-1} sec^{-1} at 164°.

The kinetic data for attack on formaldehyde confirm quantitatively what is well known qualitatively—that it possesses a methylene group of considerable reactivity toward free radicals. At 164°, *k* (cm^3 mol^{-1} sec^{-1}) is between $10^{8.95}$ and $10^{9.46}$. The reactivity reflects the low activation energy reported as 6.6 and 6.2 kcal mol^{-1}. However, the bond dissociation energy, $D(H–CHO) = 88 \pm 2$ kcal mol^{-1}, although lower than in saturated methylene compounds, is hardly consistent with such a low activation energy and it is possible that interference from secondary processes is, in part, responsible for the high rate constant (see also section 3 below).

By contrast, the CH_2 group in methylene fluoride[111] is relatively inert; at 164°, $k = 10^{5.8}$ cm^3 mol^{-1} sec^{-1}, one-tenth of the value for attack on the CH_2 group in propane. This is in accord with the high bond dissociation energy, $D(CF_2H–H) = 101 \pm 4$ kcal mol^{-1}. The Arrhenius parameters, however, show that the cause of the low reactivity compared with the CH_2 group in propane is mainly due to a lower *A* factor (*A* (cm^3 mol^{-1} sec^{-1}) is $10^{11.0}$ (methylene fluoride) and $10^{11.8}$ (propane)) since the activation energies (*E* (kcal mol^{-1}) is 10.4 for methylene fluoride and 10.2 for propane) are not significantly different.

There are few data available for attack on methylene-d_2 groups (see Table VI), but similar characteristics to those shown for attack on CH_2 groups can be distinguished.

Like the undeuterated groups, the reactivities of the methylene-d_2 groups in propane-d_2 and *n*-butane-d_4[90] are close. At 164° and on a per CD_2 group basis, both rate constants are $10^{6.0}$ cm^3 mol^{-1} sec^{-1}. Another similarity with the analogous undeuterated reactions is the similar reactivity of the methylene-d_2 in the isoelectronic pair, propane-d_2[90] and ethanol-d_2.[112] At 164°, the rate constants (in cm^3 mol^{-1} sec^{-1}) are $10^{6.0}$ for propane-d_2 and $10^{5.9}$ for ethanol-d_2. The increased reactivity of the methylene-d_2 group in ethanol-d_2 compared with its reactivity in methanol-d_3 is another example of the activating effect of the methyl group. At 164°, on a per CD_2 group basis, deuterium is abstracted some three times faster from ethanol-d_2 than from methanol-d_3.

Like the considerable reactivity of the methylene group in CH_2O, attack on the CD_2 group of formaldehyde-d_2, at 164°, has the anomalously high value[130] of $10^{8.4}$ cm^3 mol^{-1} sec^{-1}.

3. *On CH and CD Groups*

Tables VII and VIII present the kinetic data available for the attack by CH_3 (or CD_3) on CH and CD groups, respectively. In these tables some entries for methyl and methylene groups are included for comparison.

The kinetic data for methyl attack on the CH group in isobutane[90] together with data for attack on propane, ethane,[90] and methane,[90,91] show the effect on CH bond reactivity of successive substitution of methyl groups for hydrogen in methane. The results show that the methyl groups have a marked activating effect on the adjacent CH bonds: at 164°, on a per CH bond basis, the rate constants (cm^3 mol^{-1} sec^{-1}) for attack are $10^{4.1}$ and $10^{3.9}$ (methane), between $10^{5.1}$ and $10^{5.5}$ (ethane), $10^{6.5}$ (propane), and $10^{7.4}$ (isobutane). The increases in reactivity with successive methyl substitution are caused by activation energy changes from *E* (kcal mol^{-1}) = 14.2 and 14.7 for methane, 10.4, 11.7, and 11.8 for ethane,

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Table VII

Methyl Radical Attack on CH Groups

$$\mathrm{CH_3\ (or\ CD_3) + XYZ}CH \longrightarrow \mathrm{CH_4\ (or\ CD_3H) + XYZC}$$

Substrate	Radical source[a]	Temp range, °C	Log A (cm^3 mol^{-1} sec^{-1})	E, kcal mol^{-1}	Log k^b (cm^3 mol^{-1} sec^{-1}) Overall	Per CH group	Ref
$\mathrm{H_3}CH$	Acetone-d_6	350–428	11.76	14.23	4.65	4.05	90
$\mathrm{H_3{}^{14}}CH$	Acetone	200–350	11.83	14.65	4.50	3.90	91
$\mathrm{CH_3}CH\mathrm{H_2}$	Acetone-d_6	116–394	11.1	10.4	5.9	5.1	92
$\mathrm{CH_3}CH\mathrm{H_2}$	Acetone-d_6	260–490	12.17	11.73	6.30	5.52	90
$\mathrm{CD_3}CH\mathrm{H_2}$	Acetone-d_6	270–464	11.88	11.83	5.96	5.18	90
$\mathrm{(CH_3)_2H}CH$	Acetone-d_6	300–452	11.82	10.13	6.75	6.45	90
$\mathrm{(CH_3)_3}CH$	Acetone-d_6	295–456	11.38	8.03	7.36	7.36	90
$\mathrm{C_6H_5H}$	$\mathrm{Hg(CH_3)_2}$ $\mathrm{Cd(CH_3)_2}$	471–527	10.8	9.30	6.15	5.37	9
$\mathrm{CH_3H}CH\mathrm{OH}$	Acetone	130–250	11.60	9.69	6.75	6.45	112
$\mathrm{(CH_3)_2}CH\mathrm{OH}$	Acetone	135–250	11.17	7.9	7.2	7.2	66
$\mathrm{H}CH\mathrm{O}$	DTBP	122–147	11.25	6.60	8.95	8.65	129
$\mathrm{H}CH\mathrm{O}$	Azomethane	80–180	12.56	6.20	9.46	9.16	130
$\mathrm{CH_3}CH\mathrm{O}$	Azomethane	27–158	. . .	. . .	7.8	7.8	c
$\mathrm{CH_3O}CH\mathrm{O}$	Acetone	120–230	11.23	9.89	6.28	6.28	109
$\mathrm{ND_2}CH\mathrm{O}$	Acetone	123–187	10.74	7.08	7.20	7.20	68
$\mathrm{ND_2}CH\mathrm{O}$	Azomethane	144–184	~10.6	~7	~7.1	~7.1	67
$\mathrm{CF_3CHO}$	DTBP	127–171	12.10	8.70	7.75	7.75	132
$\mathrm{C_2F_5CHO}$	DTBP	127–171	12.93	9.80	8.03	8.03	132
$i\text{-}\mathrm{C_3F_7CHO}$	DTBP	127–171	13.19	10.30	7.04	7.04	132
$n\text{-}\mathrm{C_3F_7CHO}$	Acetone	127–306	11.20	5.55	8.42	8.42	133
$\mathrm{F}CH\mathrm{H_2}$	Acetone-d_6	193–331	11.2	11.8	5.3	4.8	111
$\mathrm{F_2}CH\mathrm{H}$	Acetone-d_6	122–301	11.0	10.4	5.8	5.5	111
$\mathrm{F_3}CH$	Acetone-d_6	144–309	10.4	13.56	4.7	4.7	134,135
$\mathrm{CF_3F_2}CH$	Acetone-d_6	135–318	11.94	13.56	5.2	5.2	136,135

[a] DTBP = di-*tert*-butyl peroxide. [b] At 164°. [c] Calcd from ref 118.

Table VIII

Methyl Radical Attack on CD Groups

$$\mathrm{CH_3\ (or\ CD_3) + XYZ}CD \longrightarrow \mathrm{CH_3D\ (or\ CD_4) + XYZC}$$

Substrate	Radical source	Temp range, °C	Log A (cm^3 mol^{-1} sec^{-1})	E, kcal mol^{-1}	Log k^a (cm^3 mol^{-1} sec^{-1}) Overall	Per CD group	Ref
$\mathrm{D_3}CD$	Acetone	153–428	11.25	12.93	4.78	4.18	120
$\mathrm{D_3{}^{14}CD}$	Acetone-d_6	200–350	12.61	17.8	3.7	3.1	121
$\mathrm{CD_3D_2}CD$	Acetone-d_6	260–490	12.17	13.23	5.55	4.77	90
$\mathrm{CH_3D_2}CD$	Acetone-d_6	270–464	12.03	13.73	5.16	4.38	90
$\mathrm{(CH_3)_2D}CD$	Acetone-d_6	296–420	11.81	11.53	6.04	5.75	90
$\mathrm{(CH_3)_3}CD$	Acetone-d_6	295–456	11.48	9.63	6.66	6.66	90
$\mathrm{CH_3D}CD\mathrm{OH}$	Acetone	130–250	11.61	11.40	5.91	5.61	112
$\mathrm{(CH_3)_2}CD\mathrm{OH}$	Acetone	135–250	11.28	9.69	6.43	6.43	66
$\mathrm{D}CD\mathrm{O}$	Azomethane	80–180	12.65	7.90	8.70	8.40	130
$\mathrm{NH_2}CD\mathrm{O}$	Azomethane	144–184	~10.3	~8	6.3	6.3	67
$\mathrm{CH_3O}CD\mathrm{O}$	Acetone	120–235	11.29	11.66	5.46	5.46	109

[a] At 164.

10.1 for propane, and 8.0 for isobutane. The *A* factors exhibit no particular trend and lie between $10^{11.1}$ and$10^{12.8}$ cm^{3}mol^{-1} sec^{-1}. These results are reflected by the bond dissociation energies in kcal mol^{-1} of $D(\mathrm{CH_3{-}H}) = 104 \pm 1$, $D(\mathrm{C_2H_5{-}H}) = 98 \pm 1$, $D(\mathrm{(CH_3)_2CH{-}H}) = 94.5 \pm 1$, and $D(\mathrm{(CH_3)_3C{-}H}) = 91.0 \pm 1$.

The apparent reactivity of CH in benzene[9] (at 164°, on a per CH group basis, *k* is claimed to be $10^{5.4}$ cm^3 mol^{-1} sec^{-1}) is probably spurious. A recent study[131] has produced good evidence for a high value for $D(\mathrm{C_6H_5{-}H})$ of 112 kcal mol^{-1} and direct H abstraction must be extremely rare. The reaction of benzene with methyl radicals is probably composite, comprising methyl radical addition followed by hydrogen abstraction.

The pair 2-propanol[66] and ethanol[112] reveal a similar pattern of reactivity at the α-carbon atom to the pair isobutane and propane. An eightfold increase in reactivity (per C–H bond) at 164° originates in a 1.8 kcal mol^{-1} lowering in activation energy from 9.7 kcal mol^{-1} for ethanol to 7.9 kcal mol^{-1} in 2-propanol.

A comparison of the results for attack on formalde-

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(131) D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967).

hyde[129,130] and acetaldehyde[118] shows, at 164°, a most unexpected reduction in the reactivity of the α CH bond; k ($cm^3\ mol^{-1}\ sec^{-1}$) = $10^{8.7}$ and $10^{9.2}$ (formaldehyde) and $10^{7.8}$ (acetaldehyde). This is particularly anomalous since the bond dissociation energies for D(H–CHO) and $D(CH_3CO–H)$ are both reported as 88 ± 2 kcal mol^{-1}. A further unexpected trend in reactivity is found on comparing formaldehyde and formamide[67,68] where, at 164°, the CH group in the latter is over an order of magnitude lower than in formaldehyde. Similarly, at 164°, hydrogen atoms are abstracted from the CH group in methyl formate over 200 times slower than from formaldehyde when the rate constant is expressed on a per CH bond basis. These results throw further doubt on the validity of the data for attack on formaldehyde (see section 2 above).

The results for attack on the CH group in the fluoroaldehydes,[132,133] CF_3CHO, C_2F_5CHO, $n\text{-}C_3F_7CHO$, and $i\text{-}C_3F_7CHO$, exhibit no uniform trends in rate constants or Arrhenius parameters. At 164°, all the rate constants lie in the range $10^{7.0}$–$10^{8.4}$ $cm^3\ mol^{-1}\ sec^{-1}$. It is striking that the Arrhenius parameters obtained for CF_3CHO, C_2F_5CHO, and $i\text{-}C_3F_7CHO$, using di-*tert*-butyl peroxide as radical source, are high (A factors in $cm^3\ mol^{-1}\ sec^{-1}$ lie between $10^{12.1}$ and $10^{13.1}$ and activation range from 8.7 to 10.3 kcal mol^{-1}), while Arrhenius parameters determined for attack on $n\text{-}C_3F_7CHO$ obtained using acetone as radical source are significantly lower: $A = 10^{11.2}$ $cm^3\ mol^{-1}\ sec^{-1}$ and $E = 5.6$ kcal mol^{-1}.

The kinetic data for hydrogen abstraction from mono-, di-, and trifluoromethane[111,134,135] show the CH group in trifluoromethane to be the least reactive. This is due to possession of the lowest A factor ($A = 10^{10.4}$ $cm^3\ mol^{-1}\ sec^{-1}$) and the highest activation energy ($E = 13.6$ kcal mol^{-1}), and the latter factor is in accord with the high bond dissociation energy of $D(CF_3–H) = 106 \pm 1$ kcal mol^{-1}. At 164°, on a per CH bond basis, attack on difluoromethane is greater than that on monofluoromethane by a factor of 5 originating in a lowering in activation energy from 11.8 kcal mol^{-1} (for monofluoromethane) to 10.4 kcal mol^{-1} (for difluoromethane). On this basis it would be expected that difluoromethane has the lower bond dissociation energy, although $D(FCH_2–H)$ and $D(F_2CH–H)$ are both reported as equal to 101 ± 4 kcal mol^{-1}. At 164°, abstraction from the CH group in pentafluoroethane[135,136] is some three times greater than in trifluoromethane, reflecting the lower bond dissociation energy $D(C_2F_5–H) = 103 \pm 2$ kcal mol^{-1}. It is somewhat surprising, however, that the origin of the increased reactivity lies in a threefold increase in the A factor; the activation energies are the same.

The results for attack on CD groups (Table VIII) again show similar features to those found for attack on CH groups. Like the results for the analogous undeuterated reactions, the data for abstraction of deuterium atoms from methane-d_4,[120,121] ethane-d_3, ethane-d_6, propane-d_2, and isobutane-d_1[90] show that methyl groups have a marked activating effect on the adjacent C–D bonds. At 164°, on a per CD bond basis, the reactivities increase from k ($cm^3\ mol^{-1}\ sec^{-1}$) = $10^{3.1}$ or $10^{4.1}$ for methane-d_4 to $10^{6.7}$ for isobutane-d_1. Increases in reactivity originate in activation energy changes which reflect bond dissociation energy differences.

The difference in reactivity at the α-carbon atom between 2-propanol and ethanol (see above) is paralleled in 2-propanol-d_1[66] ($(CH_3)_2CDOH$) and ethanol-d_2.[112] At 164°, on a per CD group basis, the reactivity in 2-propanol-d_1 is eight times greater than in ethanol-d_2, reflecting a lowering in activation energy of 1.7 kcal mol^{-1}.

Like the results for attack on undeuterated formaldehyde, the rate of attack on formaldehyde-d_2[130] appears anomalously high: k is reported as $10^{8.7}$ $cm^3\ mol^{-1}\ sec^{-1}$. Contrary to expectations, at 164° and on a per C–D bond basis, abstraction from formaldehyde-d_2 is greater, by a factor of *ca.* 100, than attack on formamide-d_1[67] and greater, by a factor of *ca.* 1000, than attack on methyl formate-d_1.[109]

B. ATTACK BY TRIFLUOROMETHYL RADICALS

1. On CH_3 and CD_3 Groups

Kinetic data for attack by trifluoromethyl radicals on methyl groups in different molecular environments are presented in Table IX and data for attack on methyl-d_3 groups are presented in Table X.

Several investigators[49,53,137–140] have studied the attack of trifluoromethyl radicals on methane. Hexafluoroacetone, hexafluoroazomethane, and trifluoroacetaldehyde have been used as free radical sources, and kinetic data are now available over a considerable temperature range, 30–524°. Agreement for the rate constant is fairly good and, at 164°, a value of $10^{6.4}$ $cm^3\ mol^{-1}\ sec^{-1}$ is indicated. The Arrhenius parameters are scattered: values for A range from $10^{11.2}$ to $10^{12.6}$ $cm^3\ mol^{-1}\ sec^{-1}$ and activation energies lie between 9.5 and 11.5 kcal mol^{-1}.

Reactivities toward CF_3 in methane, ethane,[53,141] and neopentane[19] show a pattern similar to that shown toward attack by methyl radicals (see section V.A1. above). At 164°, on a per CH_3 group basis, the rate constants for abstraction from methyl groups in ethane and neopentane agree within a factor of 2; k ($cm^3\ mol^{-1}\ sec^{-1}$) is $10^{7.5}$ and $10^{7.4}$ (ethane) and $10^{7.2}$ (neopentane). Both these values are higher than the corresponding one for attack on methane; $k = 10^{6.3}$ $cm^3\ mol^{-1}\ sec^{-1}$. The origin of the reactivity changes is to be found in differences in activation energy in accord with expectations based on the bond dissociation energies (kcal mol^{-1}) of 104 ± 1, 98 ± 1, and 99 ± 1 for $D(CH_3–H)$, $D(C_2H_5–H)$, and $D((CH_3)_3CCH_2–H)$, respectively.

The reactivity of methyl groups in tetramethylsilane[142] is close to that found in neopentane. At 164° k ($cm^3\ mol^{-1}\ sec^{-1}$) is $10^{8.2}$ (tetramethylsilane) and $10^{8.0}$ (neopentane), indicating similar activating effect of carbon and silicon atoms on the adjacent methyl groups.

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Table IX

Trifluoromethyl Radical Attack on Methyl Groups

$CF_3 + XCH_3 \longrightarrow CF_3H + XCH_2$

Substrate	*Radical source*[a]	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k*[b] *(cm³ mol⁻¹ sec⁻¹) Overall*	*Per CH₃ group*	*Ref*
$\mathrm{H}\mathit{CH}_3$	HFA	395–524	11.67	10.30	6.52	6.40	53
$\mathrm{H}\mathit{CH}_3$	HFAzo	30–350	11.15	9.5	6.4	6.3	138
$\mathrm{H}\mathit{CH}_3$	$\mathrm{CF_3CHO}$	162–298	11.7	10.6	6.4	6.3	49
$\mathrm{H}\mathit{CH}_3$	HFA	153–295	11.9	11.30	6.2	6.1	137
$\mathrm{H}\mathit{CH}_3$	HFA	84–310	12.6	11.0	7.1	7.0	139
$\mathrm{H}\mathit{CH}_3$	HFA	139–360	12.17	11.5	6.4	6.3	140
$\mathrm{CH_3}\mathit{CH}_3$	HFA	80–216	11.6	7.5	7.8	7.5	53
$\mathrm{CH_3}\mathit{CH}_3$	HFA	50–170	10.97	6.5	7.7	7.4	141
$\mathrm{(CH_3)_3C}\mathit{CH}_3$	HFAzo	253–315	11.75	7.6	8.0	7.2	19
$\mathrm{Si(CH_3)_3}\mathit{CH}_3$	$\mathrm{CF_3I}$	72–253	12.00	7.61	8.20	7.60	142
$\mathrm{NH_2}\mathit{CH}_3$	$\mathrm{CF_3I}$	30–162	10.72	4.17	8.63	8.63	51
$\mathrm{CH_3}\mathit{ND}\mathrm{CH_3}$	$\mathrm{CF_3I}$	30–97	11.82	5.1	9.2	8.9	52
$\mathrm{(CH_3)_2N}\mathit{CH}_3$	$\mathrm{CF_3I}$	30–162	11.82	4.5	9.5	9.0	52
$\mathrm{DO}\mathit{CH}_3$	HFAzo	134–252	12.18	8.3	8.0	8.0	143
$\mathrm{HO}\mathit{CH}_3$	$\mathrm{CF_3I}$	84–162	10.0	4.70	7.6	7.6	50
$\mathrm{CH_3O}\mathit{CH}_3$	HFA	60–180	11.71	6.78	8.32	8.02	144
$\mathrm{CD_3COO}\mathit{CH}_3$	HFA	70–220	10.06	6.81	6.65	6.65	110
$\mathrm{HCOO}\mathit{CH}_3$	HFA	114–220	11.00	8.81	6.59	6.59	109
$\mathrm{CH_3CO}\mathit{CH}_3$	HFAzo	240–315	11.50	8.0	7.5	7.2	19
$\mathrm{CH_3CO}\mathit{CH}_3$	HFA	23–240	11.51	8.27	7.37	7.07	71, 145
$\mathrm{CF_3CO}\mathit{CH}_3$	$\mathrm{CF_3COCH_3}$	13–352	11.3	6.6	8.0	8.0	146
$\mathit{CH}_3\mathrm{COOCH_3}$	HFA	60–220	10.34	5.19	7.74	7.74	110
$\mathrm{F}\mathit{CH}_3$	HFA	196–360	12.1	11.2	6.5	6.5	140
$\mathrm{CF_3}\mathit{CH}_3$	HFA	293–405	12.1	13.5	5.3	5.3	140
$\mathrm{C_6F_5}\mathit{CH}_3$	HFA	30–130	10.74	6.38	7.55	7.55	147
$\mathrm{CH_3Cl}$	HFA	144–250	12.10	10.60	6.80	6.80	137
$\mathrm{CH_3Br}$	HFA	150–260	11.62	9.90	6.67	6.67	137
$\mathrm{CH_3I}$	HFA	55–210	11.62	7.50	7.87	7.87	137

[a] HFA = hexafluoroacetone; HFAzo = hexafluoroazomethane. [b] At 164°.

Table X

Trifluoromethyl Radical Attack on Methyl-d_3 Groups

$CF_3 + XCD_3 \longrightarrow CF_3D + XCD_2$

Substrate	*Radical source*[a]	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k*[b] *(cm³ mol⁻¹ sec⁻¹) Overall*	*Per CD₃ group*	*Ref*
$\mathrm{D}\mathit{CD}_3$	HFA	106–287	11.8	12.1	5.7	5.6	139
$\mathrm{D}\mathit{CD}_3$	HFA	55–354	12.10	13.30	5.45	5.33	140
$\mathrm{H}\mathit{CD}_3$	HFA	55–354	11.8	12.75	5.4	5.4	148
$\mathrm{C_6H_5}\mathit{CD}_3$	HFA	22–72	10.1	5.8	7.2	7.2	149
$\mathrm{NH_2}\mathit{CD}_3$	$\mathrm{CF_3I}$	30–162	11.03	6.05	8.00	8.00	51
$\mathrm{HO}\mathit{CD}_3$	$\mathrm{CF_3I}$	84–162	10.20	6.61	6.89	6.89	50
$\mathrm{CH_3COO}\mathit{CD}_3$	HFA	60–220	11.82	10.52	6.56	6.56	110
$\mathit{CD}_3\mathrm{COOCH_3}$	HFA	70–220	10.38	8.79	5.98	5.98	110

[a] HFA = hexafluoroacetone. [b] At 164°.

The rate constants for abstraction from methyl groups in the amines, methylamine,[51] dimethylamine, and trimethylamine[52] are not very different. At 164°, on a per CH_3 group basis, they are (in cm³ mol⁻¹ sec⁻¹) $10^{8.63}$ (methylamine), $10^{8.9}$ (dimethylamine), and $10^{9.0}$ (trimethylamine). The rate constant for abstraction from methylamine is an order of magnitude greater than for abstraction from ethane; the enhancement in reactivity originates in lower Arrhenius parameters for attack on the amine. Similar behavior is found for attack by methyl radicals.

Kinetic data for trifluoromethyl attack on methyl groups attached to oxygen atoms are available for the substrates: methanol,[50,143] dimethyl ether,[144] methyl acetate,[110] and methyl formate.[109] At 164°, on a per CH_3 group basis, the reactivities of methyl groups in methanol and dimethyl ether are close (k (cm³ mol⁻¹ sec⁻¹) is $10^{7.6}$ and $10^{8.0}$ for methanol and $10^{8.02}$ for dimethyl ether). The reactivities in methyl acetate and methyl formate are lower by about a factor of 20 at 164°. However, the results for methyl acetate show unusual isotope effects (see section XI) and must be subject to doubt.

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(144) N. L. Arthur, P. Gray, and A. A. Herod, *Can. J. Chem.*, 47, 1347 (1969).

At 164°, the reactivity of the methyl group in methanol ($k = 10^{8.0}$ and $10^{7.6}$ cm^3 mol^{-1} sec^{-1}) is intermediate between its reactivity in the isoelectronic, ethane ($k = 10^{7.5}$ and $10^{7.4}$ cm^3 mol^{-1} sec^{-1}) and methylamine ($k = 10^{8.63}$ cm^3 mol^{-1} sec^{-1}). A similar pattern was found for attack by methyl radicals.

The kinetic data reported from the two investigations of the trifluoromethyl radical attack on acetone[19,71,145] agree closely. The Arrhenius parameters are $A = 10^{11.50}$ and $10^{11.51}$ cm^3 mol^{-1} sec^{-1} and $E = 8.0$ and 8.3 kcal mol^{-1}; and at 164°, on a per CH_3 group basis, $k = 10^{7.2}$ and $10^{7.1}$ cm^3 mol^{-1} sec^{-1}. However, the corresponding rate constant reported for attack on trifluoromethylacetone[146] is greater by a factor of 7, and the origin of the enhanced reactivity is a lowering in activation energy of 1.4 kcal mol^{-1}. These results suggest that $D(CF_3COCH_2\text{–}H)$ is significantly lower than the reported value for $D(CH_3COCH_2\text{–}H)$ of 92 ± 3 kcal mol^{-1}. The rate constant for abstraction from the acetyl methyl group in methyl acetate[110] is, at 164°, $k = 10^{7.7}$ cm^3 mol^{-1} sec^{-1}, though the result is subject to doubt (see above).

Kinetic data for trifluoromethyl radical attack on methyl groups in fluorocarbons are available for the substrates fluoromethane, trifluoromethylethane,[140] and pentafluorotoluene.[147] The results show that substitution of a fluorine atom for hydrogen in methane does not affect the reactivity of the methyl group: at 164°, on a per CH_3 group basis, the rate constants (cm^3 mol^{-1} sec^{-1}) are $10^{6.3}$ (methane) and $10^{6.5}$ (monofluoromethane). Substituting CF_3 and H in methane reduces the reactivity of the methyl group by an order of magnitude (at 164°, k is $10^{5.3}$ cm^3 mol^{-1} sec^{-1} for attack on CF_3CH_3), whereas substitution of pentafluorophenyl for hydrogen in methane has the opposite effect of increasing the CH_3 group reactivity by a factor of 20 (at 164°, $k = 10^{7.6}$ cm^3 mol^{-1} sec^{-1} for attack on $C_6F_5CH_3$).

At 164°, methyl group reactivity in the series CH_3X, where X is F, Cl, Br, and I, is greatest for attack on methyl iodide ($k = 10^{7.9}$ cm^3 mol^{-1} sec^{-1}) and least for attack on monofluoromethane ($k = 10^{6.5}$ cm^3 mol^{-1} sec^{-1}). Reported values for attack on methyl chloride and methyl bromide lie intermediate (k (cm^3 mol^{-1} sec^{-1}) is $10^{6.8}$ for methyl chloride and $10^{6.7}$ for methyl bromide). Activation energy differences are responsible for the changes in reactivity.

The trifluoromethyl radical attack on methane-d_4 has been the subject of two investigations,[139,140] and in addition the attack on methane-d_3 has been studied.[148] At 164°, the rate constants, expressed on a per CD_3 group basis, agree within a factor of 2; k (cm^3 mol^{-1} sec^{-1}) is $10^{5.6}$ and $10^{5.3}$ (methane-d_4) and $10^{5.4}$ (methane-d_3). The reported A factors (cm^3 mol^{-1} sec^{-1}) are $10^{11.8}$, $10^{12.1}$, and $10^{11.8}$, and the activation energies (kcal mol^{-1}) are 12.1, 13.3, and 12.8.

The enhanced reactivity of the methyl-d_3 group in toluene-d_3[149] shows the activating effect of the phenyl group and the stability of the benzyl radical. At 164°, deuterium is abstracted some 80 times faster from the methyl-d_3 group in toluene-d_3 than from that in methane-d_4 or methane-d_3. The increase in reactivity is wholly due to a large decrease in activation energy of about 7 kcal mol^{-1} since the reported A factor ($10^{10.1}$ cm^3 mol^{-1} sec^{-1}) is actually lower than for attack on the deuterated methanes.

The methyl-d_3 groups in methylamine-d_3[51] and methanol-d_3[50] have similar relative reactivities to their undeuterated analogs. At 164°, deuterium is abstracted over 10 times faster from methylamine-d_3 than from methanol-d_3.

The results for abstraction from CD_3 groups in methyl acetate are subject to doubt (see above).

2. *On CH_2 and CD_2 Groups*

Table XI presents kinetic data for trifluoromethyl radical attack on methylene groups. There are as yet no results published for trifluoromethyl radical attack on methylene-d_2 groups.

As for the corresponding methyl radical reactions, the methylene group reactivities in the cyclic hydrocarbons cyclopentane[19] and cyclohexane[150] are similar to one another. At 164°, on a per CH_2 group basis, the rate constant (cm^3 mol^{-1} sec^{-1}) are $10^{8.4}$ (cyclopentane) and $10^{8.2}$ (cyclohexane). Both compounds are over 100 times more reactive than methane toward attack by trifluoromethyl radicals. These superior reactivities are due to the lower activation energies ($E = 4.7$ kcal mol^{-1} for cyclopentane and 5.0 kcal mol^{-1} for cyclohexane) compared with 10.6 kcal mol^{-1} for methane. This behavior is consistent with differences in bond dissociation energies (see section V.A.2).

The methylene group reactivity in difluoromethane[140] (at 164°, $k = 10^{6.2}$ cm^3 mol^{-1} sec^{-1}) is not significantly different from the reactivity found for methane. This result parallels the result for monofluoromethane (see section 1 above) and is consistent with the reported values for $D(H\text{–}CH_3)$, $D(H\text{–}CH_2F)$, and $D(H\text{–}CHF_2)$ of 104 ± 1, and 101 ± 4, and 101 ± 4 kcal mol^{-1}, respectively.

The methylene group in dichloromethane[146] is four times more reactive toward trifluoromethyl radical attack than the methylene group in difluoromethane. The origin of the enhanced reactivity stems from both the larger A factor and the smaller activation energy found for attack on dichloromethane.

3. *On CH and CD Groups*

Table XII details kinetic data for the trifluoromethyl radical attack on tertiary CH groups in different molecular environments and Table XIII gives the kinetic data for three reactions in which tertiary CD groups are attacked.

The trifluoromethyl radical attack on two fluorocarbons containing tertiary CH groups has been studied. In both substrates, CF_2HCF_2H[140,141] and C_2F_5H,[140] the CH bond reactivity (at 164°, k (cm^3 mol^{-1} sec^{-1}) is $10^{5.8}$ or $10^{5.5}$ for CF_2HCF_2H and $10^{6.0}$ for C_2F_5H) does not differ significantly from the value of $10^{5.8}$ cm^3 mol^{-1} sec^{-1} found, at 164°, for methane. These results are consistent with the known bond dissociation energies, $D(C_2F_5\text{–}H) = 103 \pm 2$ and $D(CH_3\text{–}H) = 104 \pm 1$ kcal mol^{-1}.

The Arrhenius parameters reported for attack on pentafluoroethane ($A = 10^{11.1}$ cm^3 mol^{-1} sec^{-1} and $E = 10.1$ kcal mol^{-1}) resemble those obtained for attack on methane. The parameters reported for attack on tetrafluoroethane differ

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(145) G. O. Pritchard and J. R. Dacey, *Can. J. Chem.*, **38**, 182 (1960).

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(147) S. W. Charles, J. T. Pearson, and E. Whittle, *ibid.*, **59**, 1156 (1963).

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(149) S. W. Charles, J. T. Pearson, and E. Whittle, *Trans. Faraday Soc.*, **57**, 1356 (1961).

(150) S. W. Charles and E. Whittle, *ibid.*, **57**, 1356 (1961).

Table XI

Trifluoromethyl Radical Attack on Methylene Groups

$CF_3 + XYCH_2 \longrightarrow CF_3H + XYCH$

Substrate	*Radical source*[a]	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k*[b] *(cm³ mol⁻¹ sec⁻¹) Overall*	*Per CH₂ group*	*Ref*
$H_2\mathit{CH}_2$[c]	HFA	162–298	11.7	10.6	6.4	6.1	49
$(CH_2)_5$	HFAzo	210–300	11.54	4.7	9.1	8.4	19
$(CH_2)_6$	HFA	19–91	11.44	5.00	8.94	8.24	150
CH_2F_2	HFA	175–363	11.8	11.2	6.2	6.2	140
CH_2Cl_2	HFA	144–250	12.10	10.60	6.8	6.8	146

[a] HFA = hexafluoroacetone; HFAzo = hexafluoroazomethane. [b] At 164°. [c] Typical result.

Table XII

Trifluoromethyl Radical Attack on CH Groups

$CF_3 + XYZCH \longrightarrow CF_3H + XYZC$

Substrate	*Radical source*[a]	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k*[b] *(cm³ mol⁻¹ sec⁻¹) Overall*	*Per CH group*	*Ref*
$H_3\mathit{CH}$[c]	HFA	162–298	11.7	10.6	6.4	5.8	140
CF_2HCF_2H	HFA	50–170	7.25	2.3	6.10	5.8	141
CF_2HCF_2H	HFA	237–410	11.7	11.9	5.8	5.5	140
CF_3CF_2H	HFA	234–451	11.1	10.1	6.0	6.0	140
C_6F_5CHO	HFA	60–125	12.0	8.6	7.7	7.7	151
$Cl_3\mathit{CH}$	HFA	94–296	11.08	6.60	7.78	7.78	146
$Cl_3\mathit{CH}$	HFA	390–524	12.0	6.3	8.8	8.8	139
$\mathit{H}COOCH_3$	HFA	114–220	11.42	8.72	7.06	7.06	109
$CF_3O\mathit{CH}$	HFA	127–282	11.96	8.8	7.6	7.6	152
$C_2F_5O\mathit{CH}$	HFA	84–282	11.12	6.70	7.77	7.77	152
$i\text{-}C_3F_7O\mathit{CH}$	HFA	127–282	11.1	6.60	7.8	7.8	152

[a] HFA = hexafluoroacetone. [b] At 164°. [c] Typical result.

Table XIII

Trifluoromethyl Radical Attack on CD Groups

$CF_3 + XYZCD \longrightarrow CF_3D + XYZC$

Substrate	*Radical source*[a]	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k*[b] *(cm³ mol⁻¹ sec⁻¹) Overall*	*Per CD group*	*Ref*
D_3CD[c]	HFA	55–354	11.8	12.75	5.4	4.8	148
$(CH_3)_3\mathit{CD}$	HFA	61–207	12.48	7.4	8.8	8.8	139
$\mathit{D}COOCH_3$	HFA	114–220	11.40	10.55	6.12	6.12	109
$Cl_3\mathit{CD}$	HFA	338–537	11.78	9.0	7.3	7.3	139

[a] HFA = hexafluoroacetone. [b] At 164°. [c] Typical values.

markedly among themselves, and the low values ($A = 10^{7.3}$ cm³ mol⁻¹ sec⁻¹ and $E = 2.3$ kcal mol⁻¹) cannot be justified on any theoretical model in view of the more normal parameters obtained for this and analogous reactions. The higher parameters ($A = 10^{11.7}$ cm³ mol⁻¹ sec⁻¹ and $E = 11.9$ kcal mol⁻¹) must be preferred.

At 164°, on a per CH bond basis, abstraction from the CH group in pentafluorobenzaldehyde[151] is some 80 times faster than from methane. Although the Arrhenius parameters for attack on methane are uncertain (see Table IX), the enhanced reactivity is probably due to the lower activation energy of 8.6 kcal mol⁻¹.

The two investigations of attack by trifluoromethyl radicals on trichloromethane[139,146] performed over the temperature ranges 94–296 and 390–524° produce rate constants at 164°, differing by an order of magnitude, although both investigators reported similar values for the activation energy. Since there is a risk of radical-chain processes occurring in systems containing chlorine, it is possible that both studies may have suffered interference and a reinvestigation seems called for.

The CH group reactivities in the fluoroalkylaldehydes,[152] CF_3CHO, C_2F_5CHO, and $i\text{-}C_3F_7CHO$, agree (164°) within a factor of 2. The Arrhenius parameters for attack on C_2F_5CHO and $i\text{-}C_3F_7CHO$ are not significantly different ($A = 10^{11.1}$ cm³ mol⁻¹ sec⁻¹ and $E =$ *ca.* 6.7 kcal mol⁻¹), whereas those reported for attack on CF_3CHO are both significantly higher ($A = 10^{12.0}$ cm³ mol⁻¹ sec⁻¹ and $E = 8.8$ kcal mol⁻¹).

Trifluoromethyl radical attack on the CH bond in methyl

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(151) J. R. Majer, M. A. Naman, and J. C. Robb, *Trans. Faraday Soc.*, **65**, 3295 (1969).

(152) E. R. Morris and J. C. J. Thynne, *ibid.*, **64**, 3027 (1968).

Table XIV

Methyl Radical Attack on Amine Groups

CH_3 (or CD_3) + $XNH_2 \longrightarrow CH_4$ (or CD_3H) + XNH

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log kᵃ (cm³ mol⁻¹ sec⁻¹) Overall*	*Per NH_2 group*	*Ref*
HNH_2	Azomethane	110–180	10.8	9.8	5.9	5.7	153
HNH_2	Acetone-d_6	130–339	10.8	10.0	5.8	5.6	98
HNH_2	Acetone	144–308	10.91	10.00	5.91	5.73	100
CH_3NH_2	Azomethane	125–175	9.55	5.70	6.70	6.70	25
CD_3NH_2	Azomethane	125–175	9.77	6.00	6.77	6.77	25
$CH_3CH_2NH_2$	Azomethane	110–180	9.93	6.48	6.69	6.69	97
$NH_2(CH_2)_2NH_2$	Azomethane	90–175	10.28	6.79	6.88	6.58	78
CH_3ONH_2	Azomethane	70–190	10.70	4.53	8.43	8.43	107
CD_3CONH_2	Acetone-d_6	122–259	11.06	10.39	5.86	5.86	68
NH_2NH_2	Azomethane	110–180	11.00	5.00	8.50	8.20	153
$(CH_3)_2NNH_2$	Azomethane	112–175	11.29	5.75	8.41	8.41	89

ᵃ At 164°.

Table XV

Methyl Radical Attack on Amine-d_2 Groups

CH_3 (or CD_3) + $XND_2 \longrightarrow CH_3D$ (or CD_4) + XND

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log kᵃ (cm³ mol⁻¹ sec⁻¹) Overall*	*Per ND_2 group*	*Ref*
DND_2	Azomethane	110–180	11.0	10.9	5.5	5.3	153
CH_3ND_2	Azomethane	115–175	9.61	7.00	6.11	6.11	25
$CH_3CH_2ND_2$	Azomethane	110–180	10.04	7.64	6.22	6.22	97
$ND_2(CH_2)_2ND_2$	Azomethane	90–175	10.34	7.87	6.40	6.10	78
CH_3OND_2	Azomethane	70–190	10.55	5.88	7.61	7.61	107
ND_2ND_2	Azomethane	110–180	10.86	6.39	7.66	7.36	89
$(CH_3)_2NND_2$	Azomethane	112–175	11.33	6.82	7.92	7.92	89

ᵃ At 164°.

formate[109] is some four times slower at 164° than attack on pentafluorobenzaldehyde and on the fluoroalkylaldehydes. This is in accord with the diminished reactivity of the aldehydic hydrogen in methyl formate toward attack by methyl radicals (see Table VII).

At 164°, on a per CD bond basis, deuterium is abstracted some 10,000 times faster from isobutane-d_1[139] than from methane-d_4. The superior reactivity is due to the considerably lower activation energy ($E = 7.4$ kcal mol^{-1}) found for attack on isobutane-d_1, and this, in turn, is in accord with bond dissociation energy differences (see Appendix II).

The results[109] for abstraction from the CD bond in methyl formate-d_1 are in accord with results obtained for attack on the undeuterated substrate. At 164°, on a per CD group basis, deuterium is abstracted some 20 times faster from methyl formate-d_1 than from methane-d_4 (*cf.* a factor of 20 for the corresponding undeuterated reactions). The increase in reactivity has its origin in a lowering of the activation energy.

The results for attack on trichloromethane-d_1[139] are in some doubt owing to the conflicting rate constants reported for the analogous undeuterated reactions (see above).

VI. Abstraction from NH and ND Bonds

Some 120 reactions in which methyl or trifluoromethyl abstracts from different CH or CD bonds are listed in Tables III to XIII. In contrast, only about 25 reactions involving abstraction from NH or ND bonds have been studied. These are discussed below by considering attack on amine (NH_2) and imine (NH) groups.

A. ATTACK BY METHYL RADICALS

1. On NH_2 and ND_2 Groups

The data available for methyl attack on NH_2 and ND_2 groups in different molecular environments are presented in Tables XIV and XV, respectively.

Ammonia,[98,100,153] the first member of the amine series, is the least reactive toward attack by methyl radicals. (A parallel result is obtained for methane which is the first and least reactive member of the hydrocarbons.) At 164°, on a per NH_2 basis, the range of reactivity is covered by a factor of *ca.* 630, from $k_{164°} = 10^{5.7}$ for ammonia to $k_{164°} = 10^{8.43}$ cm^3 mol^{-1} sec^{-1} for abstraction from the amine group in *O*-methylhydroxylamine.[107]

An examination of the data for ammonia, methylamine,[25] and ethylamine[97] shows the reactivity of the amine group in molecules forming an homologous series. The effect of substituting CH_3 in ammonia is to cause an increase in the NH_2 reactivity. At 164°, hydrogen atoms are abstracted some ten

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(153) P. Gray and J. C. J. Thynne, *Trans. Faraday Soc.*, 60, 1047 (1964).

times faster from NH_2 in methylamine than from NH_2 in ammonia.

Since the A factor for abstraction from CH_3NH_2 is less than the A factor for the ammonia system, the origin of the reactivity difference lies wholly in the difference between activation energies (E = 10.8 kcal mol^{-1} for NH_3 and 5.7 or 6.0 kcal mol^{-1} for CH_3NH_2). The decrease in A factor on going from ammonia to methylamine is difficult to rationalize. In terms of accessibility one might have expected a two- to threefold reduction whereas a 12-fold reduction is found. It is of interest to note that a similar state of affairs exists for attack by CF_3 radicals (see section B.1 below).

There is no significant difference between NH_2 reactivities in methylamine and ethylamine, and the activating effects of methyl and ethyl groups are thus equal; for abstraction from the amine groups at 164°, values, in cm^3 mol^{-1} sec^{-1}, for k are $10^{6.70}$ to $10^{6.77}$ (methylamine) and $10^{6.69}$ (ethylamine).

The above rate parameters are in accord with current bond dissociation energies, $D(NH_2\text{–}H)$ = 102.5 ± 3 and $D(CH_3NH\text{–}H)$ = 92 ± 3 kcal mol^{-1}. Although no independent value is known for $D(C_2H_5NH\text{–}H)$, in view of the foregoing it is likely to be near the value of 92 ± 3 kcal mol^{-1} proposed for $D(CH_3NH\text{–}H)$.

As might be expected from the similar molecular environment, the reactivity of the amine groups in ethylenediamine[78] is similar to their reactivity in ethylamine. Rate constants, k (per NH_2 group), are close: $10^{6.58}$ for the diamine and $10^{6.69}$ cm^3 mol^{-1} sec^{-1} for ethylamine. The Arrhenius parameters are not significantly different.

When H in ammonia is replaced by methoxyl, the NH_2 reactivity is increased 500-fold.[107] This spectacular rise originates in a large drop in activation energy from 10.0 kcal mol^{-1} for NH_3 to 4.5 kcal mol^{-1} in O-methylhydroxylamine; the A factors are not significantly different.

On substituting NH_2 in ammonia, forming hydrazine, the reactivity is again greatly increased.[153] At 164°, k (per NH_2 group) is $10^{8.20}$ cm^3 mol^{-1} sec^{-1} in hydrazine compared to $10^{5.7}$ cm^3 mol^{-1} sec^{-1} in ammonia. The A factors are not significantly different and the difference in reactivity is again caused by a difference in activation energy: from *ca.* 10.0 kcal mol^{-1} for NH_3 to 5.0 kcal mol^{-1} for hydrazine. This behavior is in accord with expectations based on the bond dissociation energies: $D(NH_2\text{–}H)$ = 102.5 ± 3 and $D(N_2H_3\text{–}H)$ = *ca.* 93 kcal mol^{-1} (see Appendix II).

The difference in reactivity between the amine groups in hydrazine and in 1,1-dimethylhydrazine[89] is only marginal: at 164°, k (per NH_2 group) is $10^{8.20}$ cm^3 mol^{-1} sec^{-1} (for hydrazine) and $10^{8.41}$ cm^3 mol^{-1} sec^{-1} (for 1,1-dimethylhydrazine). This indicates similar activating effects of the NH_2 and $(CH_3)_2N$ groups.

When H in ammonia is replaced by an acetyl group, the reactivity of the NH_2 group is hardly affected.[68] At 164°, k (per NH_2 group) is *ca.* $10^{5.7}$ cm^3 mol^{-1} sec^{-1} for ammonia and $10^{5.86}$ cm^3 mol^{-1} sec^{-1} for acetamide. The Arrhenius parameters for the two systems are similar.

Trends identical with those discussed above for attack on NH_2 groups are found on inspecting the data for methyl attack on ND_2 groups (presented in Table XV).

At 164°, rate constants for attack on ND_2 in the homologous series ND_3,[153] CH_3ND_2,[25] and $C_2H_5ND_2$[97] are in the ratio 1:6:8 (*cf.* the corresponding ratio for the undeuterated species of 1:10:10). The enhanced reactivity of methylamine-d_2 and ethylamine-d_2 is again caused by lower activation energies: E = 10.9 kcal mol^{-1} (for ammonia-d_3), 7.00 kcal mol^{-1} (for methylamine-d_2), and 7.64 kcal mol^{-1} (for ethylamine-d_2). The A factor for abstraction from the amine group in methylamine-d_2 ($A = 10^{9.61}$ cm^3 mol^{-1} sec^{-1}) is again anomalously low.

The reactivities of ethylamine-d_2[97] and ethylenediamine-d_4[78] are similar: at 164°, and on a per ND_2 basis, $k = 10^{6.22}$ cm^3 mol^{-1} sec^{-1} (for ethylamine-d_2) and $10^{6.10}$ cm^3 mol^{-1} sec^{-1} (for ethylenediamine-d_4).

As for the undeuterated systems, ND_2 reactivity in O-methylhydroxylamine-d_2,[107] hydrazine-d_4,[89] and 1,1-dimethylhydrazine-d_2[89] is much greater than in ammonia-d_3. At 164°, relative to attack on ND_3, rate constants (per ND_2 group) are greater by a factor of 200 (for CH_3OND_2), 125 (for N_2D_4), and 425 (for $(CH_3)_2NND_2$).

2. *On NH and ND Groups*

Kinetic data for methyl (CH_3 or CD_3) radical attack on NH and ND groups are presented in Tables XVI and XVII, respectively. Some species containing NH_2 and ND_2 groups are included for comparison.

Data for the first three molecules listed in Table XVI illustrate the effect on the NH bond reactivity of ascending the homologous series, ammonia,[98,100,153] methylamine,[25] and dimethylamine.[126] It can be seen that the introduction of successive methyl groups enhances the reactivity of NH.

Compared with ammonia, and on a per N–H bond basis, at 164°, hydrogen is abstracted ten times more readily from the amine group in methylamine and some 160 times more readily from the amine group in dimethylamine. A comparison of the Arrhenius parameters for these reactions shows that the abstraction reaction from dimethylamine has the same A factor ($A = 10^{10.8}$ cm^3 mol^{-1} sec^{-1}) but a lower activation energy (E = 6.4 kcal mol^{-1}) than for abstraction from ammonia (E = *ca.* 10.0 kcal mol^{-1}). This is in accord with bond dissociation energy expectations; values for $D(NH_2\text{–}H)$ and $D((CH_3)_2N\text{–}H)$ of 102.5 ± 3 and 86 ± 3 kcal mol^{-1} are reported. However, methylamine owes its intermediate position not to an intermediate activation energy as would be expected from its intermediate bond dissociation energy ($D(CH_3NH\text{–}H)$ = 92 ± 3 kcal mol^{-1}) but to the low A factor ($A = 10^{9.55}$ or $10^{9.77}$ cm^3 mol^{-1} sec^{-1}). It appears to have the lowest activation energy (E = 5.7 or 6.0 kcal mol^{-1}) though the differences between these values and that for dimethylamine (E = 6.4 kcal mol^{-1}) may not be statistically significant.

It can be seen on comparing ethylenimine[101] with dimethylamine[126] that, at 164°, the NH group reactivity is enhanced by a factor of 2 in the cyclic molecule. This enhanced reactivity is due entirely to the lower activation energy for ethylenimine (E = 4.57 kcal mol^{-1}) compared with E = 6.4 kcal mol^{-1} for dimethylamine, since the A factor is 4.4 times lower for abstraction from ethylenimine.

When NH is attached to a carbonyl group in isocyanic acid the NH reactivity is drastically reduced. Woolley and Back[154] were unable to detect measurable abstraction even at 250° and we estimate from their results that, at 164°, k is approximately $10^{5.1}$ cm^3 mol^{-1} sec^{-1}; this is lower even than the rate of abstraction from ammonia (k (per NH group) = $10^{5.4}$ cm^3 mol^{-1} sec^{-1}, at 164°).

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(154) W. D. Woolley and R. A. Back, *Can. J. Chem.*, **46**, 295 (1968).

Table XVI

Methyl Radical Attack on Imine Groups

CH_3 (or CD_3) + XYNH ⟶ CH_4 (or CD_3H) + XYN

Substrate	Radical source	Temp range, °C	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k^a (cm³ mol⁻¹ sec⁻¹)*		Ref
					Overall	*Per CH_3 group*	
$H_2\mathit{NH}$	Azomethane	110–180	10.8	9.8	5.9	5.4	153
$H_2\mathit{NH}$	Acetone-d_6	130–339	10.8	10.0	5.8	5.3	98
$H_2\mathit{NH}$	Acetone	144–308	10.91	10.00	5.91	5.43	100
$CH_3\mathit{NH}$-H	Azomethane	125–175	9.55	5.70	6.70	6.40	25
$CD_3\mathit{NH}$-H	Azomethane	125–175	9.77	6.00	6.77	6.47	25
$(CH_3)_2\mathit{NH}$	Azomethane	120–175	10.81	6.40	7.61	7.61	126
$(CH_2)_2\mathit{NH}$	Azomethane	110–175	10.17	4.57	7.88	7.88	101
*HN*CO	Azomethane	250	...	...	~5.1	~5.1	154
$\mathit{HN}N_2$	Azomethane	150–180	...	...	>8.0	>8.0	155
$H_2N\mathit{NH}$H	Azomethane	110–180	11.00	5.00	8.50	7.90	89
$CH_3NH\mathit{NH}CH_3$	Azomethane	80–162	9.92	2.12	8.86	8.56	89

[a] At 164°.

Table XVII

Methyl Radical Attack on ND Groups

CH_3 (or CD_3) + XY*ND* ⟶ CH_3D (or CD_4) + XYN

Substrate	Radical source	Temp range, °C	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k^a (cm³ mol⁻¹ sec⁻¹)*		Ref
					Overall	*Per ND group*	
D_2ND	Azomethane	110–180	11.0	10.9	5.5	5.0	153
$CH_3D\mathit{ND}$	Azomethane	115–175	9.61	7.00	6.11	5.81	25
$(CH_3)_2\mathit{ND}$	Azomethane	120–175	10.65	7.80	6.75	6.75	126
$(CH_2)_2\mathit{ND}$	Azomethane	110–175	10.17	6.34	7.00	7.00	101
$ND_2\mathit{ND}D$	Azomethane	110–180	10.86	6.39	7.66	7.06	89
$CH_3ND\mathit{ND}CH_3$	Azomethane	110–180	10.00	2.88	8.56	8.26	89

[a] At 164°.

In sharp contrast is the great reactivity of NH in the isoelectronic hydrazoic acid, HN_3, where unpublished rate measurements[155] have indicated that, at 164°, k is greater than $10^{8.0}$ cm³ mol⁻¹ sec⁻¹. Bond dissociation energies for these compounds are discussed in Appendix II.

The activating effect of methyl group substitution is further illustrated on comparing hydrazine with 1,2-dimethylhydrazine.[89] On a per NH group basis, the methyl derivative is 4.6 times as reactive toward methyl attack. The enhanced reactivity is again caused solely by a reduction in activation energy (E = 2.12 kcal mol⁻¹ for dimethylhydrazine and 5.00 kcal mol⁻¹ for hydrazine). The A factor for the more reactive species is lower by a factor of 10.

The rate data available for reactions in which ND groups are attacked (see Table XVII) show similar trends to those discussed above for attack on NH groups. Thus, at 164°, rate constants for attack on ND in ND_3,[153] CH_3ND_2,[25] and $(CH_3)_2ND$[126] are in the ratio 1:6.5:56, which are to be compared with the ratios of 1:10:160 found for the undeuterated reactions. At 164°, abstraction from ND in cyclic ethylenimine[101] is faster than from dimethylamine by a factor of 1.8 (*cf.* a factor of 2 for the undeuterated reactions) due entirely to a lower activation energy: E is 6.34 kcal mol⁻¹ (ethylenimine-d_1) and 7.80 kcal mol⁻¹ (dimethylamine-d_1).

A comparison of abstraction rates from N_2D_4 and $CH_3NDNDCH_3$[89] shows that, at 164° and on a per ND group basis, abstraction from 1,2-dimethylhydrazine-d_2 is faster by a factor of 16, somewhat greater than the ratio of 4.6 found for the undeuterated systems.

B. ATTACK BY TRIFLUOROMETHYL RADICALS

1. *On NH_2 and ND_2 Groups*

Results for CF_3 attack on NH_2 groups are available for two substrates only, *viz.* ammonia[156] and methylamine-d_3.[51] These are presented in Table XVIII. They serve to illustrate the activating effect of replacing H in ammonia by CH_3. At 164°, on a per NH_2 group basis, the amine group in methylamine is 33 times more reactive than NH_2 in ammonia. The cause of the enhanced reactivity is due to the lower activation energy of 4.4 kcal mol⁻¹ for CD_3NH_2 compared with 8.3 kcal mol⁻¹ for ammonia. The A factor, though more nearly "normal," is again significantly lower for the methylamine system; $A = 10^{9.94}$ cm³ mol⁻¹ sec⁻¹ for methylamine and $10^{10.55}$ cm³ mol⁻¹ sec⁻¹ for ammonia. Parallel results were obtained for attack by methyl radicals (see section A.1 above).

Attack by trifluoromethyl on ammonia-d_3[156] provides the only available results for attack on an ND_2 group. They are presented in Table XVIII. The A factor, $A = 10^{10.47}$ cm³ mol⁻¹

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(155) A. Jones and J. C. J. Thynne, unpublished work, 1969.

(156) P. Gray, N. L. Arthur, and A. C. Lloyd, *Trans. Faraday Soc.*, **65**, 775 (1969).

Table XVIII

Trifluoromethyl Radical Attack on Amine and Amine-d_2 Groups

$$CF_3 + XNH_2 \longrightarrow CF_3H + XNH$$

$$CF_3 + XND_2 \longrightarrow CF_3D + XND$$

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k[a] (cm³ mol⁻¹ sec⁻¹)*		*Ref*
					Overall	*Per amine group*	
$H\mathit{NH}_2$	CF_3I	113–240	10.55	8.29	6.40	6.22	156
$CD_3\mathit{NH}_2$	CF_3I	30–162	9.94	4.39	7.74	7.74	51
$D\mathit{ND}_2$	CF_3I	113–240	10.47	9.35	5.81	5.63	156

[a] At 164°.

Table XIX

Trifluoromethyl Radical Attack on Imine and Imine-d_1 Groups

$$CF_3 + XYNH \longrightarrow CF_3H + XYN$$

$$CF_3 + XYND \longrightarrow CF_3D + XYN$$

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k[a] (cm³ mol⁻¹ sec⁻¹)*		*Ref*
					Overall	*Per imine group*	
$H_2\mathit{NH}$	CF_3I	113–240	10.55	8.29	6.40	5.92	156
$CH_3H\mathit{NH}$	CF_3I	30–162	9.94	4.39	7.74	7.44	51
$(CH_3)_2\mathit{NH}$	CF_3I	30–97	10.5	3.3	8.8	8.8	52
$(CH_2)_2\mathit{NH}$	CF_3I	30–162	11.00	4.1	8.9	8.9	52
$D_2\mathit{ND}$	CF_3I	113–240	10.47	9.35	5.79	5.31	156
$(CH_3)_2\mathit{ND}$	CF_3I	50–97	10.9	4.7	8.5	8.5	52

[a] At 164°.

sec⁻¹, and activation energy, $E = 9.4$ kcal mol⁻¹, are both in the expected range.

2. On NH and ND Groups

There are, in essence, only two investigations of abstraction from NH groups, *viz.* attack on dimethylamine and on ethylenimine,[52] and these are presented in Table XIX along with the ammonia and methylamine results for comparison. The results for ammonia, methylamine, and dimethylamine demonstrate the effect on the NH reactivity toward CF_3 attack of substituting CH_3 for H in ammonia. As is found in the analogous attack by methyl radicals (see section A.2 above), the reactivity of the NH group increases markedly in methylamine and dimethylamine. At 164°, and on a per N–H bond basis, compared with ammonia the amine group in methylamine is 33 times more reactive and the imine group in dimethylamine is 800 times more reactive. For attack by methyl radicals the corresponding reactivity ratios are 10 (methylamine) and 160 (dimethylamine).

In accord with bond dissociation energy expectations ($D(NH_2\text{–}H)$, $D(CH_3NH\text{–}H)$, and $D((CH_3)_2N\text{–}H)$ are 102.5 ± 3, 92 ± 3, and 86 ± 3 kcal mol⁻¹, respectively), the activation energies, kcal mol⁻¹, show a gradation from $E = 8.3$ (ammonia) through $E = 4.4$ (methylamine) to $E = 3.3$ (dimethylamine).

By assuming that the attack on ethylenimine is predominantly at the NH position, Morris and Thynne[52] have estimated the appropriate rate parameters. They show that NH group reactivity is similar to that in dimethylamine (at 164°, $k = 10^{8.8}$ and $10^{8.9}$ cm³ mol⁻¹ sec⁻¹, respectively). Although the activation energy increased from 3.3 kcal mol⁻¹ for dimethylamine to 4.1 kcal mol⁻¹ for ethylenimine, the A factors compensated by increasing from $A = 10^{10.5}$ for dimethylamine to $10^{11.0}$ cm³ mol⁻¹ sec⁻¹ for ethylenimine.

The results for the CF_3 attack on dimethylamine-d_1 and ammonia-d_3 (see Table XIX) show, once again, the inertness of ammonia. At 164°, and on a per N–D bond basis, deuterium is abstracted some 1600 times slower from ammonia-d_3 than from dimethylamine-d_1.

VII. Abstraction from OH, OD, SH, and SD Bonds

There are kinetic data for only ten reactions involving methyl and trifluoromethyl attack on alcohols, alkanethiols, and their deuterated derivatives. This is partly due to the experimental difficulties experienced in the investigation of many of these compounds; hydroxyl groups are relatively inert over the usual temperature ranges used, whereas sulfide groups are extremely reactive. Neither situation is conducive to the determination of accurate rate data (see section II).

A. ABSTRACTION FROM OH AND OD GROUPS

1. Attack by Methyl Radicals

All the investigations of attack on alcohols (see Table XX) have used acetone as the source of CH_3 or CD_3 radicals. An isotopic exchange reaction[66] between alcohols and acetone restricts the number of compatible pairs to CH_3COCH_3 + ROH or CD_3COCD_3 + ROD. The effect is to permit the best conditions for studying abstraction from alkyl groups but to deny the best conditions for studying abstraction from hydroxyl groups.

Table XX

Methyl Radical Attack on OH and OD Groups (Eq a and b) and Trifluoromethyl Radical Attack on OH Groups (Eq c)

$$CH_3 \text{ (or } CD_3) + XOH \longrightarrow CH_4 \text{ (or } CD_3H) + XO \text{ (a)}$$

$$CD_3 + XOD \longrightarrow CD_4 + XO \text{ (b)}$$

$$CF_3 + XOH \longrightarrow CF_3H + XO \text{ (c)}$$

Substrate	*Radical source*^{a}	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k^b (cm^3 mol^{-1} sec^{-1})*	*Ref*
$H\mathit{OH}$	Calculated from data for reverse reaction		12.65	20.0	2.7	157
$CD_3\mathit{OH}$	Acetone	135–250	10.5	9.5	5.7	66
$CD_3\mathit{OH}$	Acetone	133–200	9.25	6.40	6.05	102
$CD_3\mathit{OH}$	Acetone-d_6	125–245	10.46	9.00	5.96	103
$CH_3CH_2\mathit{OH}$	Acetone-d_6	130–250	10.90	9.40	6.20	112
$CH_3\mathit{OD}$	Acetone-d_6	140–250	10.5^c	~11.3	4.8	66
$CH_3CH_2\mathit{OD}$	Acetone-d_6	130–250	10.79	10.15	5.71	112
$CH_3\mathit{OH}$	HFAzo	134–252	11.18	8.3	7.03	143
$CD_3\mathit{OH}$	CF_3I	84–162	9.48	3.24	7.86	50

^{a} HFAzo = hexafluoroazomethane. ^{b} At 164°. ^{c} Assumed.

For abstraction from methanol, the results[66] of Gray and Herod ($A = 10^{10.5}$ cm^3 mol^{-1} sec^{-1} and $E = 9.5$ kcal mol^{-1}) are probably to be preferred. The two other investigations are subject to doubt: one,[103] because acetone-d_6 was used as radical source, where isotopic exchange may have invalidated the results, and the other,[102] because of an anomalously low A factor ($10^{9.25}$ cm^3 mol^{-1} sec^{-1}) and an activation energy ($E = 6.4$ kcal mol^{-1}) inconsistent with bond dissociation energy expectations.

Water, methanol, and ethanol form the first three members of the primary alcohol homologous series. The data show that as the series is ascended the reactivity of the OH group increases. At 164°, and on a per OH bond basis, k (cm^3 mol^{-1} sec^{-1}) is $10^{2.4}$ (for water), $10^{5.7}$ (for methanol), and $10^{6.2}$ (for ethanol).

The kinetic data calculated for water[157] show that the origin of the relatively slow rate of attack lies in the large activation energy ($E = 20$ kcal mol^{-1}). The 2000-fold increase in reactivity found for OH in methanol is caused entirely by a decrease in activation energy to a value, $E = 9.5$ kcal mol^{-1}, since the A factor is also lower than the value for water (A (cm^3 mol^{-1} sec^{-1}) $= 10^{12.7}$ for water and $10^{10.5}$ for methanol). The smaller enhancement of reactivity found for ethanol appears to be caused by an increase in A factor, from $10^{10.5}$ cm^3 mol^{-1} sec^{-1} (for methanol) to $10^{10.9}$ cm^3 mol^{-1} sec^{-1} (for ethanol) though the difference is probably not significant in view of experimental errors. The rate constants and activation energies are broadly in line with expectations based on the known bond dissociation energies (kcal mol^{-1}): $D(\text{HO–H}) = 119 \pm 1$, $D(\text{CH}_3\text{O–H}) = 102 \pm 2$, and $D(\text{C}_2\text{H}_5\text{O–H}) = 102 \pm 2$.

An investigation[66] of the methyl radical attack on 2-propanol, aimed at extending our knowledge of the OH reactivity in the above series, was unable to furnish reliable kinetic data for attack at the OH position owing to interference by a secondary reaction (see section II.D).

The results[66,112] for abstraction of deuterium atoms from OD groups in methanol-d_1 and ethanol-d_1 are given in Table XX. Over the temperature range 140–250°, abstraction of D from CH_3OD is so slow that it is almost completely masked by abstraction from the radical source, acetone-d_6. Consequently, a precise determination of Arrhenius parameters is not possible. However, by assuming that the A factor is the same as that for abstraction from OH in CH_3OH ($A = 10^{10.5}$ cm^3 mol^{-1} sec^{-1}), Gray and Herod[66] estimated an activation energy of 11.3 kcal mol^{-1}.

As for the analogous undeuterated species, the deuteroxyl group in ethanol-d_1 is more reactive than in methanol-d_1; at 164°, D is abstracted eight times faster from C_2H_5OD than from CH_3OD. The origin of this enhanced reactivity probably lies in the lower activation energy found for abstraction from C_2H_5OD (E (kcal mol^{-1}) $= 10.2$ (C_2H_5OD) and *ca.* 11.3 (CH_3OD)).

2. *Attack by Trifluoromethyl Radicals*

The two determinations[50,143] of the CF_3 attack on the OH group in methanol given in Table XX constitute the only results available for abstraction from OH or OD groups. The results obtained using hexafluoroacetone as radical source and those obtained using trifluoromethyl iodide are in wide disagreement. The rate constants, at 164°, differ by a factor of 7, the A factors by a factor of 50, and the activation energies by 5 kcal mol^{-1}. Further investigation is clearly necessary to resolve the conflict, and such an investigation would probably benefit by using a radical source other than hexafluoroacetone or trifluoromethyl iodide (see section II). With our present knowledge, we would prefer the results of Cotton, Steeper, and Christenson[143] on the grounds that these authors report the more "normal" Arrhenius parameters ($A = 10^{11.2}$ cm^3 mol^{-1} sec^{-1} and $E = 8.3$ kcal mol^{-1}).

B. ABSTRACTION FROM SH AND SD GROUPS

1. *Attack by Methyl Radicals*

The results for hydrogen abstraction by methyl radicals from S–H and S–D bonds are summarized in Table XXI. Few substrates have been studied to date.

Hydrogen sulfide has received most attention. Results have been reported using methyl radicals generated from azo-

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(157) D. Garvin, Ed., N.B.S. Report No. 9884, U. S. Department of Commerce, Washington D. C., 1969.

Table XXI

Methyl and Trifluoromethyl Radical Attack on SH and SD Bonds

$$CH_3 + XSH \longrightarrow CH_4 + XS$$

$$CH_3 + D_2S \longrightarrow CH_3D + DS$$

$$CF_3 + H_2S \longrightarrow CF_3H + HS$$

$$CF_3 + D_2S \longrightarrow CF_3D + DS$$

Substrate	*Radical source*[a]	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k*[b] *(cm³ mol⁻¹ sec⁻¹)*	*Ref*
H*SH*	Azomethane	99–171	10.7	2.9	9.3	158
H*SH*	Acetone	50–200	11.4	2.6	10.1	159
H*SH*	Acetaldehyde	150–360	12.1	3.5	10.3	69, 33
CD_3*SH*	Acetone	127–203	11.03	4.10	8.98	69
D*SD*	Acetaldehyde	260–316	12.2	4.5	9.9	69, 160
H*SH*	HFA	63–100	11.6	3.9	9.6	161
H*SH*	HFA	60–100	11.81	4.19	9.61	162
H*SH*	HFA	95–161	11.2	1.20	10.6	163
D*SD*	HFA	60–100	11.90	4.93	9.43	162

[a] HFA = hexafluoroacetone. [b] At 164°.

methane,[158] acetone,[159] and acetaldehyde.[33,160] The azomethane work ($A = 10^{10.7}$ cm³ mol⁻¹ sec⁻¹, $E = 2.9$ kcal mol⁻¹) is preferred. Questions of interference by secondary reactions cast doubts on the studies based on acetaldehyde[33,160] since the decomposition of acetaldehyde in the presence of thiols is known to be complex; in the study based on acetone, secondary reactions may have interfered, and no account was taken of the nonlinearity of the Arrhenius temperature dependence for attack by methyl radicals on acetone. At 164°, the results based on azomethane yield a value for k of $10^{9.3}$ cm³ mol⁻¹ sec⁻¹, whereas the earlier results based on acetone and acetaldehyde yielded rate constants, at 164°, of *ca.* $10^{10.3}$ cm³ mol⁻¹ sec⁻¹. The occurrence of an apparently normal kinetic isotope effect ($A_H/A_D = 0.75$, $E_D - E_H = 1.15$ kcal mol⁻¹, and $k_H/k_D = 2.5$ at 164°) in the work with acetaldehyde[160] is of little consequence, since a normal isotope effect has been found for methyl radical attack on the OH group of 2-propanol[66] although secondary reactions are known to occur there. A reinvestigation of H_2S and D_2S is clearly called for.

At 164°, the rate constants reported for the CH_3 attack on the SH group of methyl mercaptan[69] is $10^{9.0}$ cm³ mol⁻¹ sec⁻¹ which is identical with the rate constant for abstraction from H_2S when expressed on a per S–H group basis. For abstraction from CH_3SH both the A factor ($A = 10^{11.0}$ cm³ mol⁻¹ sec⁻¹) and the activation energy (4.1 kcal mol⁻¹) for attack on the SH group are greater than for attack on H_2S ($A = 10^{10.7}$ cm³ mol⁻¹ sec⁻¹ and $E = 2.9$ kcal mol⁻¹); the similar rate constants at 164° thus arise from compensating effects of the Arrhenius parameters. This result is unusual since comparisons of the rates of attack on the substrate pairs CH_4–CH_3-CH_3, NH_3–CH_3NH_2, and H_2O–CH_3OH show that abstraction from the functional group is markedly greater for the methyl-substituted derivatives. The similarity of the rate constants at 164° is consistent with reported bond dissociation energies[76] (D(HS–H) = 90 ± 2 and D(CH_3S–H) = 88 kcal mol⁻¹). In view of the similarities in bond dissociation energies, the difference of 1.2 kcal mol⁻¹ in activation energy for CH_3SH and H_2S must be regarded with suspicion.

2. *Attack by Trifluoromethyl Radicals*

Results are available for CF_3 attack on H_2S and D_2S only, and these are summarized in Table XXI.

The H_2S system has been the subject of three investigations,[161–163] all three of which used hexafluoroacetone as the free radical source. The Arrhenius parameters obtained from two of the investigations[161,162] agree closely ($A = 10^{11.6}$ and $10^{11.8}$ cm³ mol⁻¹ sec⁻¹; $E = 3.9$ and 4.2 kcal mol⁻¹) and must be preferred at this stage.

The results for D_2S[162] are discussed in section XI.

VIII. Abstraction from Members of Isoelectronic Series

The groups CH_3, NH_2, and OH are isoelectronic, as are CH_2 and NH. It is to be expected that when these groups (or their deuterated derivatives) are placed in similar molecular environments they may show similar reactivities. The examination below of a number of isoelectronic series shows, however, that bond dissociation energies are a major influence on reactivities.

A. ABSTRACTION FROM CH_3, NH_2, AND OH (AND CD_3, ND_2, AND OD) GROUPS

1. *Attack by Methyl Radicals*

Table XXII presents the data for the methyl radical attack on the isoelectronic series methane, ammonia, and water. At 164°, attack on ammonia is by far the most rapid; on a per atom basis, hydrogen atoms are abstracted some 25 times faster from ammonia than from methane and some 600 times faster than from water. Since the attack on ammonia has the lowest A factor, the superior reactivity has its origin in the lower activation energy of 10 kcal mol⁻¹. (Values for attack

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(158) P. Gray, A. A. Herod, and L. J. Leyshon, *Can. J. Chem.*, **47**, 689 (1969).

(159) N. Imai and O. Toyama, *Bull. Chem. Soc. Jap.*, **33**, 652 (1960).

(160) N. Imai, T. Dohmaru, and O. Toyama, *ibid.*, **38**, 639 (1965).

(161) N. L. Arthur and T. N. Bell, *Can. J. Chem.*, **44**, 1445 (1966).

(162) N. L. Arthur and P. Gray, *Trans. Faraday Soc.*, **65**, 434 (1969).

(163) J. D. Kale and R. B. Timmons, *J. Phys. Chem.*, **72**, 4239 (1968).

Table XXII

Methyl Radical Attack on the Isoelectronic Groups CH_3, NH_2, and OH and Their Deuterated Derivatives

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k^a (cm^3 mol^{-1} sec^{-1})*		*Ref*
					Per group	*Per atom*	
$\mathrm{H}CH_3$	Acetone-d_6	350–428	11.76	14.23	4.52	4.04	90
$\mathrm{H}^{14}CH_3$	Acetone	200–350	11.83	14.65	4.38	3.90	91
$\mathrm{H}NH_2$	Azomethane	110–180	10.8	9.8	5.7	5.4	153
$\mathrm{H}NH_2$	Acetone-d_6	130–339	10.8	10.0	5.6	5.3	98
$\mathrm{H}NH_2$	Acetone	144–308	10.91	10.00	5.73	5.43	100
$\mathrm{H}\text{-}OH$	Calculated from data for reverse reaction		12.65	20.0	2.6	2.6	157
$\mathrm{D}CD_3$	Acetone	153–428	11.25	12.93	4.66	4.18	120
$\mathrm{D}^{14}CD_3$	Acetone-d_6	200–350	12.61	17.8	3.59	3.11	121
$\mathrm{D}ND_2$	Azomethane	110–180	11.0	10.9	5.3	5.0	153

[a] At 164°.

Table XXIII

Methyl Radical Attack on the Isoelectronic Groups CH_3, NH_2, and OH and Their Deuterated Derivatives

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k^a (cm^3 mol^{-1} sec^{-1})*		*Ref*
					Per group	*Per atom*	
$\mathrm{CH_3}CH_3$	Acetone-d_6	116–394	11.1	10.4	5.6	5.1	92
$\mathrm{CH_3}CH_3$	Acetone-d_6	260–490	12.17	11.73	6.00	5.52	90
$\mathrm{CH_3}CH_3$	Acetone-d_6	270–464	11.88	11.83	5.96	5.48	90
$\mathrm{CH_3}NH_2$	Azomethane	125–175	9.55	5.70	6.70	6.40	25
$\mathrm{CD_3}NH_2$	Azomethane	125–175	9.77	6.00	6.77	6.47	25
$\mathrm{CD_3}OH$	Acetone	135–250	10.5	9.5	5.7	5.7	66
$\mathrm{CD_3}OH$	Acetone	133–200	9.25	6.40	6.05	6.05	102
$\mathrm{CD_3}OH$	Acetone-d_6	125–245	10.46	9.00	5.96	5.96	103
$\mathrm{CD_3}CD_3$	Acetone-d_6	260–490	12.17	13.23	5.25	4.77	90
$\mathrm{CH_3}CD_3$	Acetone-d_6	270–464	12.03	13.73	5.16	4.68	90
$\mathrm{CH_3}ND_2$	Azomethane	115–175	9.61	7.00	6.11	5.81	25
$\mathrm{CH_3}OD$	Acetone-d_6	140–250	~10.5	~11.3	~6.0	~6.0	66

[a] At 164°.

on methane and water are 14.4 and 20 kcal mol^{-1}, respectively.)

Although the large difference in reactivity between ammonia and methane is somewhat surprising, these reactivities reflect the bond dissociation energies of 104 ± 1, 102.5 ± 3, and 119 ± 1 kcal mol^{-1} reported for $D(CH_3\text{–}H)$, $D(NH_2\text{–}H)$, and $D(HO\text{–}H)$, respectively.

Kinetic data for the analogous deuterated reactions, methyl attack on methane-d_4 and ammonia-d_3, are also presented in Table XXII. Although the data for attack on methane-d_4 are not good (the two rate constants reported at 164° differ by a factor of 10), they show the same effect as the undeuterated species. At 164°, on a per atom basis, attack on ammonia-d_3 is faster by a factor of approximately 20 and both A factor and activation energy are lower for attack on ammonia-d_3.

Table XXIII presents the data for methyl radical attack on the CH_3, NH_2, and OH groups in the series ethane, methylamine, and methanol. Reaction rates and Arrhenius parameters for attack on the groups show similar features to those found for attack on them in methane, ammonia, and water. However, attack on methanol at the OH group is faster than attack on the CH_3 group in ethane. The amine group is again the most reactive due to the lowest activation energy of 5.7 or 6.0 kcal mol^{-1}. At 164°, on a per atom basis, the rate constants for attack on the NH_2, OH, and CH_3 groups are in the approximate ratio 10:3:1. The lower activation energy found for attack on the amine group is consistent with the low value of 92 ± 3 kcal mol^{-1} reported for $D(CH_3NH\text{–}H)$. It is surprising, however, that the reactivities and activation energies reported for attack on ethane and methanol (E (kcal mol^{-1}) is 11.8 for ethane and 9.5 for methanol) are in a reverse order to those expected on the basis of the bond dissociation energies of 98.0 ± 1 and 102 ± 2 kcal mol^{-1} reported for $D(C_2H_5\text{–}H)$ and $D(CH_3O\text{–}H)$.

Disregarding the results for methyl attack on the OD group in methanol-d_1 which are only approximate, the data for attack on the analogous deuterated compounds exhibit similar features (see Table XXIII). The CD_3 group in ethane-d_3 or ethane-d_6 is the least reactive; at 164°, on a per atom basis, the rate constant is smaller than that for attack on the amine by a factor of 10. Both Arrhenius parameters for attack on the methylamine-d_2 are less than those for attack on the deuterated ethanes.

An identical state of affairs is found for methyl attack on CH_3, NH_2, and OH groups in the series propane, ethylamine, and ethanol (see Table XXIV). On a per atom basis, the rate constants at 164° for attack on NH_2, OH, and CH_3 are in the ratio 8:5:1 (*cf.* the ratio 10:3:1 for attack on the same groups in the series ethane, methylamine, and methanol). The superior reactivity of the amine group toward methyl radical attack is due to the low activation energy (E = 6.5 kcal mol^{-1}) compared with the values (kcal mol^{-1}) of 9.4 and 11.5 reported for attack on ethanol and propane. The reactivities and activation energies for attack on the OH and CH_3 groups

Table XXIV

Methyl Radical Attack on the Isoelectronic Groups CH_3, NH_2, and OH and Their Deuterated Derivatives

Substrate	Radical source	Temp range, °C	Log *A* (cm³ mol⁻¹ sec⁻¹)	*E*, kcal mol⁻¹	Log *k*[a] (cm³ mol⁻¹ sec⁻¹)		Ref
					Per group	Per atom	
$CH_3CD_2\mathit{CH}_3$	Acetone-d_6	296–420	12.04	11.53	5.97	5.49	90
$CH_3CH_2\mathit{NH}_2$	Azomethane	110–180	9.93	6.48	6.69	6.39	97
$CH_3CH_2\mathit{OH}$	Acetone-d_6	130–250	10.90	9.40	6.20	6.20	112
$CH_3CH_2\mathit{ND}_2$	Azomethane	110–180	10.04	7.64	6.22	5.92	97
$CH_3CH_2\mathit{OD}$	Acetone-d_6	130–250	10.79	10.15	5.71	5.71	112

[a] At 164°.

Table XXV

Methyl Radical Attack on the Isoelectronic Groups CH_3 and NH_2 and Their Deuterated Derivatives

Substrate	Radical source	Temp range, °C	Log *A* (cm³ mol⁻¹ sec⁻¹)	*E*, kcal mol⁻¹	Log *k*[a] (cm³ mol⁻¹ sec⁻¹)		Ref
					Per group	Per atom	
$CH_3O\mathit{CH}_3$	$Hg(CH_3)_2$	100–250	10.8	8.4	6.3	5.8	104
$CH_3O\mathit{CH}_3$	Acetone	108–198	11.3	9.5	6.2	5.7	98
$CH_3O\mathit{CH}_3$	CH_3OCH_3[b]	25–292	11.6	10.0	6.3	5.8	105
$CH_3O\mathit{CH}_3$	CH_3OCH_3[b]	200–300	11.06	9.4	6.1	5.6	106
$CH_3O\mathit{CH}_3$	Acetone	135–250	11.6	10.0	6.3	5.8	66
$CH_3O\mathit{NH}_2$	Azomethane	70–190	10.70	4.53	8.45	8.13	107

[a] At 164°. [b] Mercury ($^3P_1$) photosensitized decomposition.

in ethanol and propane are again inconsistent with the known bond dissociation energies. $D(CH_3CH_2CH_2–H) = 98 \pm 2$ kcal mol⁻¹ and $D(CH_3CH_2O–H) = 102 \pm 2$ kcal mol⁻¹. The lower activation energy for attack on ethylamine indicates a bond dissociation energy, $D(CH_3CH_2NH–H)$, lower than 98 kcal mol⁻¹. The results for attack on the deuterated analogs, ethylamine-d_2 and ethanol-d_1 (see Table XXIV), are in line with those for the undeuterated species. At 164°, on a per atom basis, deuterium atoms are abstracted 1.6 times faster from the ND_2 group in ethylamine-d_2 than from the OD group in ethanol-d_1, reflecting a lowering in activation energy of 2.6 kcal mol⁻¹.

Table XXV presents results for methyl radical attack on the isoelectronic pair dimethyl ether and *O*-methylhydroxylamine, CH_3OCH_3 and CH_3ONH_2. The characteristics shown by the rate parameters for the series above are again exhibited here. At 164°, on a per atom basis, attack on the NH_2 group in *O*-methylhydroxylamine is faster by a factor of *ca.* 250 than attack on the CH_3 group in dimethyl ether, and again the origin of the superior reactivity for attack on the amine is an activation energy lower by *ca.* 5.0 kcal mol⁻¹. On the basis of the patterns exhibited by the above series we can predict Arrhenius parameters for attack on the OH group in methyl peroxide of $A = ca.\ 10^{11.8}$ cm³ mol⁻¹ sec⁻¹ and $E = ca.\ 9.5$ kcal mol⁻¹.

The pattern of reactivities is unexpectedly reversed when the kinetic data for methyl radical attack on the isoelectronic pair, acetone and acetamide, are considered (see Table XXVI). At 164°, on a per atom basis, attack on the NH_2 group in acetamide is slower than attack on the CH_3 group in acetone by a factor of 2. The origin of this decrease in reactivity is the greater activation energy (*E* (kcal mol⁻¹) is 10.9 for acetamide and between 9.5 and 9.9 for acetone) coupled with a smaller *A* factor for attack on acetamide.

2. *Attack by Trifluoromethyl Radicals*

Table XXVII gives the data available for the trifluoromethyl attack on the isoelectronic pair methane and ammonia. At 164°, on a per atom basis, the rate of attack on ammonia is not significantly different from the rate of attack on methane: *k* (cm³ mol⁻¹ sec⁻¹) is $10^{5.9}$ (NH_3) and $10^{5.8}$ (CH_4). This is in marked contrast to the results for methyl radical attack (Table XXII) where at 164°, on a per atom basis, attack on ammonia was greater by a factor of *ca.* 25. The similar reactivity arises from a compensatory effect in the Arrhenius parameters which are both much lower for attack on ammonia. It is noteworthy that the reactivities, at 164°, are consistent with the bond dissociation energies, $D(CH_3–H) = 104 \pm 1$ and $D(NH_2–H) = 102.5 \pm 3$ kcal mol⁻¹. However, if, in view of the experimental error, the bond strengths are close, the large difference in the reported activation energies (for attack on methane *E* is 9.5–11.5 kcal mol⁻¹ and for attack on ammonia *E* is 8.3 kcal mol⁻¹) is unexpected. The results for trifluoromethyl radical attack on the corresponding deuterated substrates (see Table XXVII) show, at 164°, on a per atom basis, that the ND_2 group in ammonia-d_3 is more reactive than the CD_3 group in methane-d_4 by a factor of approximately 2.5. The small increase in reactivity is again due to a large (between 2.7 and 3.9 kcal mol⁻¹) difference in activation energies.

The results for CF_3 attack on the CH_3, NH_2, and OH groups of ethane, methylamine, and methanol are given in Table XXVIII. Some features of the pattern shown by the data for methyl attack on this series (Table XXIII) can be distinguished. The amine group is the most reactive and the Arrhenius parameters for attack on it ($A = 10^{9.94}$ cm³ mol⁻¹ sec⁻¹ and $E = 4.4$ kcal mol⁻¹) are both significantly lower than those for attack on the other members of the series (disregarding the anomalously low Arrhenius parameters reported[50]

Table XXVI

Methyl Radical Attack on the Isoelectronic Groups CH_3 and NH_2 and Their Deuterated Derivatives

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k[a] (cm³ mol⁻¹ sec⁻¹) Per group*	*Per atom*	*Ref*
$\mathrm{CH_3CO}\mathit{CH_3}$	Acetone	129–248	11.46	9.64	6.34	5.86	112
$\mathrm{CH_3CO}\mathit{CH_3}$	Acetone	122–253	11.35	9.53	6.28	5.80	113
$\mathrm{CH_3CO}\mathit{CH_3}$	Acetone	100–300	11.52	9.72	6.36	5.88	23
$\mathrm{CH_3CO}\mathit{CH_3}$	Acetone	113–300	11.53	9.87	6.29	5.81	114
$\mathrm{CD_3CO}\mathit{NH_2}$	Acetone-d_6	136–257	11.06	10.89	5.86	5.56	68

[a] At 164°.

Table XXVII

Trifluoromethyl Radical Attack on the Isoelectronic Groups CH_3 and NH_2 and Their Deuterated Derivatives

Substrate	*Radical source[a]*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k[b] (cm³ mol⁻¹ sec⁻¹) Per group*	*Per atom*	*Ref*
$\mathrm{H}\mathit{CH_3}$	HFA	395–524	11.67	10.30	6.4	5.9	53
$\mathrm{H}\mathit{CH_3}$	HFAzo	30–350	11.15	9.5	6.3	5.8	138
$\mathrm{H}\mathit{CH_3}$	CF_3CHO	162–298	11.7	10.6	6.3	5.8	49
$\mathrm{H}\mathit{CH_3}$	HFA	153–295	11.9	11.30	6.1	5.6	137
$\mathrm{H}\mathit{CH_3}$	HFA	84–310	12.0	11.0	6.4	5.9	139
$\mathrm{H}\mathit{CH_3}$	HFA	139–360	12.17	11.5	6.3	5.8	140
$\mathrm{H}\mathit{NH_2}$	CF_3I	113–240	10.55	8.29	6.22	5.92	156
$\mathrm{H}\mathit{CD_3}$	HFA	55–354	11.8	12.75	5.3	4.8	148
$\mathrm{D}\mathit{CD_3}$	HFA	106–287	11.8	12.1	5.6	5.1	139
$\mathrm{D}\mathit{CD_3}$	HFA	139–360	12.10	13.30	5.33	4.85	140
$\mathrm{D}\mathit{ND_2}$	CF_3I	113–240	10.47	9.35	5.61	5.31	156

[a] HFA = hexafluoroacetone; HFAzo = hexafluoroazomethane. [b] At 164°.

Table XXVIII

Trifluoromethyl Radical Attack on the Isoelectronic Groups CH_3, NH_2, and OH and Their Deuterated Derivatives

Substrate	*Radical source[a]*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k[b] (cm³ mol⁻¹ sec⁻¹) Per group*	*Per atom*	*Ref*
$\mathrm{CH_3}\mathit{CH_3}$	HFA	80–216	11.6	7.5	7.5	7.0	53
$\mathrm{CH_3}\mathit{CH_3}$	HFA	50–170	10.97	6.5	7.4	6.9	1
$\mathrm{CD_3}\mathit{NH_2}$	CF_3I	30–162	9.94	4.39	7.74	7.44	51
$\mathrm{CH_3}\mathit{OH}$	HFAzo	134–252	11.18	8.3	7.0	7.0	143
$\mathrm{CD_3}\mathit{OH}$	CF_3I	84–162	9.48	3.24	6.24	6.24	50

[a] HFA = hexafluoroacetone; HFAzo = hexafluoroazomethane. [b] At 164°.

Table XXIX

Methyl Radical Attack on the Isoelectronic Groups CH_2 and NH, and CD_2 and ND

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm³ mol⁻¹ sec⁻¹)*	*E, kcal mol⁻¹*	*Log k[a] (cm³ mol⁻¹ sec⁻¹) Per group*	*Per atom*	*Ref*
$\mathrm{(CH_3)_2}\mathit{CH_2}$	Acetone-d_6	300–452	11.82	10.13	6.75	6.45	90
$\mathrm{(CH_3)_2}\mathit{NH}$	Azomethane	120–175	10.81	6.40	7.61	7.61	126
$\mathrm{(CH_3)_2}\mathit{CD_2}$	Acetone-d_6	296–420	11.81	11.53	6.04	5.74	90
$\mathrm{(CH_3)_2}\mathit{ND}$	Azomethane	120–175	10.65	7.80	6.75	6.75	126

[a] At 164°.

for attack on methanol). At 164°, on a per atom basis, the rate constants for attack on the NH_2 group in methylamine and the CH_3 group in ethane are in the ratio *ca.* 3:1 which can be compared with the corresponding ratio of *ca.* 10:1 for attack by methyl radicals. In contrast to the result for methyl radical attack, however, the OH group appears to be marginally the least reactive when attacked by trifluoromethyl radicals though the two results for this reaction are too contradictory to make definite assertions.

B. ABSTRACTION FROM CH_2 AND NH (AND CD_2 AND ND) GROUPS

Comparisons of isoelectronic pairs in this section are restricted by the availability of data to attack by methyl radicals.

Table XXIX gives the kinetic results for attack on the CH_2 and NH groups in propane[90] and dimethylamine.[126] At 164°, on a per atom basis, hydrogen atoms are abstracted 14 times faster from the NH group in dimethylamine than from the

Table XXX

Methyl Radical Attack on the Isoelectronic Groups CH_2 and NH

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k^a (cm^3 mol^{-1} sec^{-1})* Per group	Per atom	*Ref*
$\overline{CH_2CH_2\mathit{CH_2}}$	Acetone-d_6	139–292	11.0	10.3	5.3	5.0	98
$\overline{CH_2CH_2\mathit{CH_2}}$	$Hg(CH_3)_2$	100–250	11.1	10.2	5.5	5.2	104
$\overline{CH_2CH_2\mathit{CH_2}}$	Acetone-d_6	248–404	11.7	13.1	4.6	4.3	122
$\overline{CH_2CH_2\mathit{NH}}$	Azomethane	110–175	10.17	4.57	7.88	7.88	101, 127
$\overline{CD_2CD_2\mathit{NH}}$	Acetone	100–216	10.76	5.28	8.12	8.12	164

[a] At 164°.

Table XXXI

Methyl Radical Attack on the Isoelectronic Groups CH_2 and NH, and CD_2 and ND

Substrate	*Radical source*	*Temp range, °C*	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*Log k^a (cm^3 mol^{-1} sec^{-1})* Per group	Per atom	*Ref*
$CH_3(\mathit{CH_2})_2CH_3$	Acetone-d_6	250–450	11.87	9.53	6.80	6.50	90
$CH_3(\mathit{NH})_2CH_3$	Azomethane	80–162	9.92	2.12	8.56	8.56	89
$CH_3(\mathit{CD_2})_2CH_3$	Acetone-d_6	356–450	12.08	11.54	6.01	5.71	90
$CH_3(\mathit{ND})_2CH_3$	Azomethane	110–180	10.00	2.88	8.36	8.36	89

[a] At 164°.

CH_2 group in propane. The origin of the superior reactivity lies in the lower activation energy since the *A* factor for attack on the imine group is also lower. The reactivities and activation energies are in accord with expectations based on the reported bond dissociation energies: $D((CH_3)_2CH\text{-}H)$ = 94.5 ± 1 kcal mol^{-1} and $D((CH_3)_2N\text{-}H)$ = 86 ± 3 kcal mol^{-1}. The rate parameters for attack on the deuterated analogs (Table XXIX) show an identical pattern. At 164°, on a per atom basis, the ND group in dimethylamine-d_1 is ten times more reactive than the CD_2 group in propane-d_2, reflecting an activation energy difference of 3.7 kcal mol^{-1}.

Kinetic data for the cyclic isoelectronic pair, cyclopropane[98,104,122] and ethylenimine,[101,127,164] are presented in Table XXX. A pattern identical with that shown for attack on propane and dimethylamine is apparent. At 164°, on a per atom basis, attack at the NH group in ethylenimine is faster, by a factor of *ca.* 1000, than attack at the CH_2 group in cyclopropane. The enhanced reactivity is again due to a lower activation energy (for attack on cyclopropane *E* is reported as 10.3, 10.2, and 13.1 kcal mol^{-1} and for attack on ethylenimine values of 4.6 and 5.3 kcal mol^{-1} have been obtained). The results indicate that the bond dissociation energy for the NH bond, $D(C_2H_2N\text{-}H)$, is significantly lower than the value of 101 ± 3 kcal mol^{-1} reported for $D(C_3H_5\text{-}H)$.

A similar pattern to that shown above is exhibited by the kinetics of attack on the CH_2 and NH groups in the isoelectronic pair, *n*-butane[90] and 1,2-dimethylhydrazine[89] (see Table XXXI). On a per atom basis, at 164°, abstraction from the NH groups is faster by a factor of 100 than abstraction from the CH_2 groups due to a much lower activation energy. The large activation energy difference of 7.4 kcal mol^{-1} indicates a bond dissociation energy for the NH bond in 1,2-dimethylhydrazine significantly lower than the CH bond strength in *n*-butane; $D(CH_3CH_2(CH_3)CH\text{-}H)$ is 94.6 ± 1 kcal mol^{-1}. The kinetic data for attack on the deuterated analogs (Table XXXI) are in line with expectations. On a per atom basis, at 164°, the ND groups in 1,2-dimethylhydrazine-d_2 are some 450 times greater in reactivity than the CD_2 groups in *n*-butane-d_4, reflecting the large difference in the activation energies of 8.6 kcal mol^{-1}.

IX. Radical Attack at Specific Sites within Molecules

We consider in this section the results for some 20 substrates for which the kinetics of radical attack at specific sites within the molecules have been elucidated. Table XXXII presents data for attack by methyl radicals and Table XXXIII presents data for attack by trifluoromethyl radicals.

A. ABSTRACTION BY METHYL RADICALS

1. Attack on Hydrocarbons

The data in Table XXXII indicate that attack on CH_2 or CH groups is much faster than on CH_3 groups. For the three hydrocarbons, propane, *n*-butane, and isobutane,[90] at 164°, attack on the CH_3 groups accounts for 25, 12, and 10%, respectively, of the overall reaction. This variation in relative reactivity is revealed even more clearly by considering the reactivity per atom. In propane, the hydrogen atoms of the methylene group are ten times more reactive than those of the methyl groups. In *n*-butane, a molecule similar to propane in consisting only of methyl and methylene groups, the hydrogen atoms of the methylene groups are 11 times more reactive than those of the methyl groups. Isobutane, however, shows a different picture; the hydrogen atom of the CH group is approximately 80 times more reactive than the hydrogen atoms of the

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(164) R. F. Klemm, *Can. J. Chem.*, 43, 2633 (1965).

Table XXXII

Methyl Radical Attack on Specific Sites within Molecules

Substrate	*Log k (164°)*	*Rel reactivities*	*Log k (164°) per atom*	*Rel reactivities per atom*	*A-factor ratio per atom*	*Ref*
$\mathit{CH}_3\mathrm{CD_2CH_3}$	6.27	1	5.49	1	1	90
$\mathrm{CH_3}\mathit{CH}_2\mathrm{CH_3}$	6.75	3.0	6.45	9.1	1.8	90
$\mathit{CH}_3\mathrm{CD_2CD_2CH_3}$	6.23	1	5.45	1	1	90
$\mathrm{CH_3}\mathit{CH}_2\mathit{CH}_2\mathrm{CH_3}$	7.10	7.4	6.50	11.2	1	90
$(\mathit{CH}_3)_3\mathrm{CD}$	6.41	1	5.46	1	1	90
$\mathrm{(CH_3)_3}\mathit{CH}$	7.36	8.9	7.36	79.5	1.4	90
$\mathit{CH}_3\mathrm{ND_2}$	6.65	1	6.17	1	15.8	25
$\mathrm{CD_3}\mathit{NH}_2$	6.77	1.3	6.47	2.0	1	25
$\mathit{CD}_3\mathrm{NH_2}$	5.81	1	5.33	1	11.8	25
$\mathrm{CH_3}\mathit{ND}_2$	6.11	2.0	5.81	3.0	1	25
$(\mathit{CH}_3)_2\mathrm{ND}$	7.11	1	6.33	1	1	126
$\mathrm{(CH_3)_2}\mathit{NH}$	7.61	3.2	7.61	19.1	1.3	126
$\mathrm{CH_3}\mathit{CH}_2\mathrm{NH_2}$	7.11	2.6	6.81	2.6	17.4	97
$\mathrm{CH_3CH_2}\mathit{NH}_2$	6.69	1	6.39	1	1	97
$\mathit{CH}_3\mathrm{CH_2NH_2}$	~5.8	~0.13	~5.3	~0.08	. . .	97
$(\mathit{CH}_2)_2\mathrm{ND}$	6.3	1	5.7	1	4.3	101, 127
$\mathrm{(CH_2)_2}\mathit{NH}$	7.88	38.0	7.88	151	1	101
$\mathrm{ND_2}\mathit{CH}_2\mathit{CH}_2\mathrm{ND_2}$	7.27	2.4	6.67	2.4	4.5	78
$\mathit{NH}_2\mathrm{CH_2CH_2}\mathit{NH}_2$	6.88	1	6.28	1	1	78
$\mathrm{(CH_3)_2N}\mathit{NH}_2$	8.41	12.6	8.11	32	~6	89
$(\mathit{CH}_3)_2\mathrm{NND_2}$	7.4	1	6.6	1	1	89
$\mathit{CH}_3\mathrm{NDND}\mathit{CH}_3$	~8.3	1	~7.5	1	~16	89
$\mathrm{CH_3}\mathit{NHNH}\mathrm{CH_3}$	8.86	3.6	8.56	11	1	89
$\mathit{CH}_3\mathrm{OND_2}$	6.3	1	5.8	1	. . .	107
$\mathrm{CH_3O}\mathit{NH}_2$	8.43	135	8.13	214	. . .	107
$\mathit{CH}_3\mathrm{CONH_2}$	5.83	1	5.35	1	1	68
$\mathrm{CD_3CO}\mathit{NH}_2$	5.86	1.07	5.56	1.6	1.7	68
$\mathit{CH}_3\mathrm{OD}$	6.26	3.6	5.78	1.2	2.0	66
$\mathrm{CD_3}\mathit{OH}$	5.7	1	5.7	1	1	66
$\mathit{CD}_3\mathrm{OH}$	5.37	3.7	4.89	1.2	~2.3	66
$\mathrm{CH_3}\mathit{OD}$	4.8	1	4.8	1	1	66
$\mathrm{CH_3}\mathit{CH}_2\mathrm{OH}$	6.75	3.5	6.45	1.8	2.5	112
$\mathrm{CH_3CH_2}\mathit{OH}$	6.20	1	6.20	1	1	112
$\mathit{CH}_3\mathrm{CH_2OH}$	~5.6	~0.25	~5.1	~0.08	. . .	112
$\mathrm{(CH_3)_2}\mathit{CH}\mathrm{OH}$	7.2	3.2	7.2	3.2	. . .	66
$\mathrm{(CH_3)_2CH}\mathit{OH}$	6.69	1	6.69	1	. . .	66
$\mathrm{DCOO}\mathit{CH}_3$	5.55	1	5.07	1	1	109
$\mathit{H}\mathrm{COOCH_3}$	6.28	4.3	6.28	16.3	~43	109
$\mathrm{CD_3COO}\mathit{CH}_3$	5.30	1	4.82	1	1	110
$\mathit{CH}_3\mathrm{COOCD_3}$	6.34	11	5.86	11.0	1.1	110
$\mathit{CD}_3\mathrm{COOCH_3}$	3.88	1	3.40	1	1.4	110
$\mathrm{CH_3COO}\mathit{CD}_3$	5.44	36	4.96	36	1	110
$\mathit{CH}_3\mathrm{CDO}$	7.0	1	6.5	1	. . .	118
$\mathrm{CH_3}\mathit{CHO}$	7.8	6.3	7.8	20	. . .	118

methyl groups. In each case, the difference in reactivity is a consequence of the enhanced reactivity of the CH_2 or CH groups since the methyl groups in these three molecules show equal reactivity ($k = 10^{5.94}$ cm^3 mol^{-1} sec^{-1} per methyl group). These differences in reactivity reflect differences in bond dissociation energies at the different sites in the molecules: $D(\mathrm{C_2H_5CH_2{-}H}) - D[\mathrm{(CH_3)_2CH{-}H}] = D(\mathrm{C_3H_7CH_2{-}H}) - D[\mathrm{C_2H_5(CH_3)CH{-}H}] =$ *ca.* 3–4 kcal mol^{-1}, while $D\,[\mathrm{(CH_3)_2CHCH_2{-}H}] - D[\mathrm{(CH_3)_3C{-}H}] =$ *ca.* 7 kcal mol^{-1}. In so far as ratios of *A* factors are significantly different from unity, they imply that the methyl groups are somewhat less accessible to attack than are either the CH_2 or the CH groups.

2. *Attack on Amines*

Attack on the methyl group of methylamine[25] is slower than attack on either the NH_2 group or the CH_2 groups of the primary amines, ethylamine[97] and ethylenediamine.[78] At 164° in methylamine, 43% of methyl radical attack is at the methyl group and the remaining 57% is at the amine group. In the deuterated species, 33% comes from the CD_3 group and 67% from the ND_2 group. The changed percentages reflect the difference in kinetic isotope effects at the two sites.

In ethylamine and ethylenediamine, at 164°, 27 and 29.5%, respectively, of attack is on the NH_2 groups, and 72 and 71%, respectively, at the CH_2 groups. Only about 2% of the attack on ethylamine is at the methyl group which shows a reactivity similar to that shown by methyl groups in hydrocarbons. These results indicate that in methylamine the CH bond dissociation energy $\mathrm{D}(\mathit{H}\mathrm{{-}CH_2NH_2})$ is greater than the value of 92 ± 3 kcal mol^{-1} reported for $D(\mathrm{CH_3NH{-}H})$. The bond dissociation energies of the methylene C–H bonds in ethylamine are probably less than the value of 92 ± 3 kcal mol^{-1} expected

Table XXXIII

Trifluoromethyl Radical Attack on Specific Sites

Substrate	*Log k (164°)*	*Rel reactivities*	*Log k (164°) per atom*	*Rel reactivity per atom*	*A-factor ratio per atom*	*Ref*
$\mathit{CH}_3\mathrm{NH}_2$	8.63	7.8	8.15	5.1	4.0	51
$\mathrm{CD}_3\mathit{NH}_2$	7.74	1	7.44	1	1	51
$(\mathit{CH}_3)_2\mathrm{ND}$	9.2	2.5	8.4	1	3.5	52
$(\mathrm{CH}_3)_2\mathit{NH}$	8.8	1	8.8	2.5	1	52
$\mathit{CH}_3\mathrm{OD}$	8.0	9.3	7.5	3.0	50	143
$\mathrm{CH}_3\mathit{OH}$	7.03	1	7.03	1	1	143
$\mathit{CH}_3\mathrm{OH}$	7.6	1	7.1	1	16.6	50
$\mathrm{CD}_3\mathit{OH}$	7.86	1.8	7.86	5.7	1	50
$\mathrm{DCOO}\mathit{CH}_3$	6.59	1	6.11	1	1	109
$\mathit{H}\mathrm{COOCH}_3$	7.06	3.0	7.06	8.9	5.2	109
$\mathit{CH}_3\mathrm{COOCD}_3$	7.74	12.3	7.26	12.3	1.9	110
$\mathrm{CD}_3\mathrm{COO}\mathit{CH}_3$	6.65	1	6.17	1	1	110
$\mathit{CD}_3\mathrm{COOCH}_3$	5.98	1	5.50	1	1	110
$\mathrm{CH}_3\mathrm{COO}\mathit{CD}_3$	6.56	3.8	6.08	3.8	27.6	110

for the NH bond strengths in these compounds (see Appendix II).

The *A* factors for attack at the different sites in the primary amines indicate that the amine groups are significantly less accessible to attack by methyl radicals. Low *A* factors are found for attack on amine groups while *A* factors for attack on CH bonds are similar to those found for hydrocarbons.

In the two secondary amines, dimethylamine[126] and ethylenimine,[101,127] the NH group is the more reactive; at 164°, 76% of attack is at the NH bond in dimethylamine, while in ethylenimine attack on the NH bond accounts for 97% of the total reaction. At 164° and on a per atom basis, hydrogen attached to nitrogen in dimethylamine is 19 times more reactive than hydrogen attached to carbon, whereas in ethylenimine, hydrogen attached to nitrogen is approximately 150 times as reactive as hydrogen attached to carbon.

The superior relative reactivity of the imine groups in dimethylamine and ethylenimine is probably a consequence of N–H bond dissociation energies lower than those in primary amines. (The N–H bond strength in dimethylamine is some 3 kcal mol^{-1} lower than that found in methylamine.) However, the high percentage of attack at the imine group in ethylenimine is partly due to the inertness of the methylene groups. On a per atom basis, the ratio of *A* factors ($A_{\mathrm{NH}}/A_{\mathrm{CH}_3} = 1.3$), if significantly greater than unity, indicates that the methyl groups in dimethylamine are rather less accessible to attack than the imine group. For attack on the imine group in ethylenimine a low *A* factor is found in line with those found for attack on the primary amines.

The NH bonds in the substituted hydrazines[89] are extremely reactive: at 164°, 78% of the attack on 1,2-dimethylhydrazine and 93% of the attack on 1,1-dimethylhydrazine being on the NH bonds. At the same temperature and on a per atom basis, hydrogen is abstracted from the NH bonds in 1,2-dimethylhydrazine 11 times faster than from CH bonds; in 1,1-dimethylhydrazine the amine hydrogen is abstracted 32 times faster than the hydrogen of the methyl groups.

In *O*-methylhydroxylamine,[107] methyl radical attack occurs almost exclusively at the amine position and, at 164°, less than 0.5% of attack is at the methyl group. This is probably due to a low N–H bond dissociation energy but partly a consequence of an unreactive methyl group which has similar reactivity to that in propane.

Methyl radical attack on acetamide[68] shows a somewhat different pattern in that, at 164°, the methyl and amine groups are equally reactive (52% of the radical attack is at the amine group and 48% at the methyl group). Both groups are between 500 and 1000 times less reactive than in 1,1-dimethylhydrazine. On a per atom basis, the ratio of *A* factors ($A_{\mathrm{NH}_2}/A_{\mathrm{CH}_3} = 1.7$) indicates that the amine group is more accessible to attack.

3. *Attack on Alcohols, Esters, and Aldehydes*

The data for attack on methanol[66] indicate that, at 164°, 78% of the attack is at the alkyl group. On a per atom basis, however, the alkyl hydrogen atoms are only 1.2 times as reactive as the hydroxyl hydrogen atom; the same relative reactivities are found for the deuterated methanols.

Ethanol[112] is attacked mainly at the methylene group. At 164°, 74% of the abstraction occurs there, 21% at the hydroxyl group, and the remaining 5% at the methyl group. On a per atom basis at 164°, the methylene hydrogen atoms are 1.8 times as reactive as the methyl group hydrogen atoms. On a per atom basis, the ratio of *A* factors for attack at the methylene and hydroxyl groups ($A_{\mathrm{CH}_2}/A_{\mathrm{OH}}$) is 2.5, indicating the greater accessibility of the methylene group to attack by methyl radicals.

Of the esters, the results for methyl formate[109] indicate that, at 164°, the formyl hydrogen atom is very reactive, 81% of the reaction being at this site. At 164°, on a per atom basis, the formyl hydrogen atom is 16 times more reactive than the hydrogen atoms of the methoxyl group. This difference in reactivity of the two sites is partly a consequence of the depressed reactivity of the methoxyl group which is less reactive than the methyl groups in ethane. The large ratio ($A_{\mathrm{CH}}/A_{\mathrm{CH}_3}$ = *ca.* 43) indicates that the formyl hydrogen is much more accessible to attack by methyl radicals.

In methyl acetate,[110] a similar pattern to that found for methyl formate is revealed. At 164° the acetyl group is the more reactive, 91% of the abstraction being from this site. As in methyl formate, the methoxyl group is unreactive, and this is mainly responsible for the large difference in reactivity between the acetyl and methoxyl groups. The *A* factors for attack at the two sites are not significantly different. However, for attack on the deuterated species, the order of reactivities of the two groups appears to be reversed with 97% of the abstraction taking place at the methoxyl group. This dramatic and inexplicable reversal throws further doubt on the validity of the experimental results for this substrate (see also sections V and XI).

Acetaldehyde[118] contains a fairly reactive methyl group and an extremely reactive acyl hydrogen atom; at 164°, 86% of the reaction is at the acyl hydrogen and, on a per atom basis, the acyl site is 20 times more reactive than the methyl hydrogen atoms. The bond strength $D(\mathrm{CH_3CO{-}H})$ is reported[76] as 88 ± 2 kcal mol^{-1}, and on this basis the bond strength $D(\mathrm{H{-}CH_2CHO})$ is expected to be about 92 kcal mol^{-1}, similar to the value reported for acetone.

B. ABSTRACTION BY TRIFLUOROMETHYL RADICALS

1. *Attack on Amines*

Only methylamine[51] and dimethylamine[52] have been investigated, and the results are summarized in Table XXXIII. The results for methylamine show that, at 164°, 88% of the reaction takes place at the methyl group and 12% at the amine group. At 164°, on a per atom basis, the CH bond is five times more reactive than the NH bond. This contrasts sharply with the corresponding results for attack by methyl radicals where, at the same temperature, the N–H bond was found to be twice as reactive as the CH bond. The reasons for this change are considered further in section X. On a per atom basis the ratio of A factors for attack at the different sites (A_{CH_3}/A_{NH_2}) is 5.1 indicating that the methyl group is the more accessible toward trifluoromethyl attack; the corresponding ratio for attack by methyl radicals was 15.8.

In dimethylamine, the methyl groups are again more reactive than the NH group, at 164°, some 71% of the reaction taking place at the methyl groups. However, on a per atom basis, the NH bond is some 2.5 times more reactive than the CH bond. This result can be compared with the corresponding one for attack by methyl radicals where it was found that, on a per atom basis, the NH bond was more reactive by a factor of almost 20.

2. *Attack on Alcohols and Esters*

Two different investigations of trifluoromethyl radical attack on methanol have been made. The rate constants and Arrhenius parameters are not in agreement. The results of one investigation[143] suggest that, at 164°, 90% of the abstraction takes place at the methyl group, whereas the second investigation[50] found only 35% of the abstraction at this site. Further work is necessary to clarify this situation.

The results for methyl formate[109] indicate that attack predominates at the formyl hydrogen position (75% of the total attack at 164°). At the same temperature and on a per atom basis, the formyl CH bond is nine times more reactive than the CH bonds of the methoxyl group. Expressed on a per atom basis, the A factor ratio ($A_{CH}/A_{OCH_3} = 5.2$) reflects a more accessible approach to the formyl site.

The results for methyl acetate[110] show similar anomalies to those discussed above for attack by methyl radicals. At 164°, 93% of the reaction occurs at the acetyl group. In the deuterated molecules, however, the methoxyl group appears to be the more reactive site and investigation of the separate rate constants suggests that this is a result of an unusually large isotope effect at the acetyl group ($k_H/k_D = 57$ at 164°) and an unusually small isotope effect at the methoxyl group ($k_H/k_D = 1.2$ at 164°). Further investigation of both methyl and trifluoromethyl radical attack on this substrate is required.

X. *Comparison of the Reactivities of Methyl and Trifluoromethyl Radicals*

A. RESUMÉ OF PRINCIPAL EXPERIMENTAL RESULTS

The purpose of this section is to compare rate constants and Arrhenius parameters for the reactions of methyl and trifluoromethyl radicals with the same substrates. For convenience of presentation the reactions are grouped into those involving attack on (a) CH and CD bonds, (b) NH and ND bonds, and (c) other bonds.

Because the reactions being compared often involve different investigators using different experimental techniques, the errors attached to the rate parameters in Tables XXXIV and XXXV can be large. Systematic errors often cancel when considering reactions involving attack by one radical species but may reveal themselves when reactions of different radical species are compared.

1. *Attack on CH and CD Bonds*

The data for methyl and trifluoromethyl radical attack on CH bonds are summarized in Table XXXIV. Four general features are apparent.

Table XXXIV

Comparison of Reactivities of CH_3 and CF_3 Radicals toward CH and CD Bonds

Substrate	A_{CF_3}/A_{CH_3}	$E_{CH_3} - E_{CF_3}$, *kcal mol⁻¹*	k_{CF_3}/k_{CH_3} *(164°)*	*Reference* CH_3	*Reference* CF_3
CH_4	0.24–2.6	2.7–4.7	32–74	90	49, 53, 137–140
CD_4	3.2	0.8	6.3	120	139
CD_4	7.1	−0.4	3.8	120	140
CD_4	0.2	5.7	100	20	139
CD_4	0.3	4.5	55	20	140
C_2H_6	0.3	4.2	32	90	53
C_2H_6	0.1	5.2	25	90	1
$(CH_3)_3\mathit{CD}$	10	2.2	126	90	139
$(CH_3)_4C$	3.2	2.4	50	92	19
$(CH_3)_4C$	4.0	2.8	80	93	19
$(CH_3)_4C$	0.26	4.4	47	94	19
$Si(CH_3)_4$	2.2	3.0	71	165	165
$Si(CH_3)_4$	1.1	3.1	43	165	165
$Si(CH_3)_4$	3.1	2.7	63	96	142
$(CH_2)_5$	0.3	4.3	32	124	19
$(CH_2)_6$	0.1	4.5	16	125	19
$C_6H_5\mathit{CD}_3$	0.02	5.5	13	95	149
CH_3F	0.8	0.6	16	111	140
CH_2F_2	6.3	−0.8	25	109	140
CH_3NH_2	0.4	4.8	96	25	51
CD_3NH_2	1.5	4.1	155	25	51
$(\mathit{CH}_3)_2ND$	2.3	3.6	125	126	52
$(CH_3)_3N$	0.8	44	130	100	52
CH_3OD	7.8	1.8	50	66	143
CH_3OH	0.05	5.4	20	66	50
CD_3OH	0.07	5.3	33	66	50
CH_3OCH_3	1.3	3.2	50	66	144
CH_3COCH_3	1.1	1.4	5.5	112	71, 145
$HCOO\mathit{CH}_3$	9.8	0.1	11.5	109	109
$\mathit{H}COOCH_3$	1.5	1.2	6.0	109	109
$\mathit{D}COOCH_3$	1.3	1.1	4.6	109	109
CF_3CHO	0.4	0.3	0.6	132	49
CF_3CHO	0.7	−0.1	0.6	132	152
C_2F_5CHO	0.02	3.1	0.6	132	152
C_3F_7CHO	0.008	3.7	0.6	132	152
CH_3COOCD_3	0.12	4.66	25	110	110
$CH_3COO\mathit{CD}_3$	2.2	1.53	12	110	110
CD_3COOCH_3	0.06	6.66	126	110	110
$CD_3COO\mathit{CH}_3$	0.07	5.05	23	110	110

(a) Abstractions by trifluoromethyl radicals are nearly always faster than abstractions by methyl radicals; at 164°, the reactivity ratio (k_{CF_3}/k_{CH_3}) is usually greater than unity and can be as large as 150.

(b) The superior reactivity of the trifluoromethyl radical is mainly a result of lower activation energies. Abstractions by trifluoromethyl radicals commonly require some 3 kcal mol^{-1} less activation energy than the corresponding methyl reactions. (However, the errors attached to these activation energy differences are typically ± 0.5 kcal mol^{-1} and in some cases could be as large as ± 1.0 kcal mol^{-1}.)

(c) The *A*-factor ratios show no particular trend and are scattered fairly evenly about unity. Since individual *A* factors can be in error by a factor of 2, few of the ratios are significantly different from unity.

(d) The fluoroalkyl aldehydes[49,132,152] at present form the notable exceptions to the general trend. For attack on these, the rate constant quotient (k_{CF_3}/k_{CH_3}) is less than unity, a consequence of low values for A_{CF_3}/A_{CH_3} rather than of unfavorable activation energy differences.

No trend in values of k_{CF_3}/k_{CH_3} is revealed with increasing methyl substitution of methane; at 164°, rate constant ratios for attack on methane,[53,49,90,137-140] ethane,[1,53,90] *tert*-butane,[90,130] and neopentane[19,92-94] are widely scattered between 4 and 126. Rate constant quotients at 164°, which lie between 4 and 155, are obtained for attack on CH and CD bonds in hydrocarbons, fluoromethanes,[109,111,140] amines,[25,51,52,100,126] methanol,[50,66,143] dimethyl ether,[66,144] acetone,[71,112,145] methyl formate,[109] methyl acetate,[110] and tetramethylsilane.[96,142,165]

2. *Attack on NH and ND Bonds*

Kinetic data are available (see Table XXXV) for the methyl and trifluoromethyl radical attack on NH and ND bonds in ammonia,[100,156] ammonia-d_3,[153,156] methylamine-d_3,[25,51] dimethylamine, and dimethylamine-d_1.[52,126] Four features of interest can be noted: (a) trifluoromethyl radical attack is faster than methyl attack as was found for attack on hydrocarbons; (b) trifluoromethyl radical attack becomes increasingly faster than methyl radical attack as the degree of substitution of the amine increases [at 164°, k_{CF_3}/k_{CH_3} is 3.1 and 1.7 (NH_3 and ND_3), 9.3 (CD_3NH_2), and 16 and 63 ($(CH_3)_2NH$ and $(CH_3)_2ND$)]; (c) the enhanced reactivity is a result of activation energy differences ($E_{CH_3} - E_{CF_3}$ is in the range 2.5-3.1 kcal mol^{-1}); (d) the ratios of *A* factors are unity within the probable experimental errors.

Table XXXV

Comparison of the Reactivities of CH_3 and CF_3 Radicals toward NH, OH, and Other Bonds

Substrate	A_{CF_3}/A_{CH_3}	$E_{CH_3} - E_{CF_3}$, kcal mol^{-1}	k_{CF_3}/k_{CH_3} (*164°*)	*Reference* *CH₃*	*CF₃*
NH_3	0.4	1.7	3.1	100	156
ND_3	0.5	1.5	1.7	153	156
$CD_3\mathit{NH}_2$	1.5	1.6	9.3	25	51
$(CH_3)_2\mathit{NH}$	0.5	3.1	16	126	52
$(CH_3)_2\mathit{ND}$	1.6	3.1	63	126	52
$CD_3\mathit{OH}$	5	1.2	20	66	143
$CD_3\mathit{OH}$	0.5	2.9	16	66	50
H_2S	13	−1.3	2.5	158	162
H_2S	10	−1.0	2.5	158	161
D_2S	0.5	0.4	0.3	69, 160	162
HCl	0.6	−3.0	0.02	169	162
HCl	0.4	−2.8	0.02	169	170
HBr	0.1	−1.5	0.02	171	170, 172
HI	0.17	1.8	1.3	173	174
HI	0.13	0.8	0.3	175	174
SiH_4	1.2	1.8	8.0	142	196
$\mathit{HSi}(CH_3)_3$	6.9	2.3	100	142	96
$HSiCl_3$	0.05	1.7	0.4	166	168
$HSiCl_3$	8.7	−1.7	1.2	167	167

3. *Attack on Other Bonds*

The data are listed in Table XXXV. The following points are of interest: (a) many of the *A* factors are the same within the errors; (b) the ratios of rate constants indicate that, at 164°, trifluoromethyl radical attack is faster than methyl radical attack on silanes[96,142,166-168] but that methyl radical attack is faster on hydrogen halides[162,169-175] and hydrogen sulfide;[158,161,162] (c) activation energy differences ($E_{CH_3} - E_{CF_3}$) lie between 0 and 3 kcal mol^{-1} for abstraction from the silanes and hydrogen iodide but are negative for attack on hydrogen chloride, hydrogen bromide, and hydrogen sulfide.

Methyl substitution of silane appears to enhance the reactivity of the Si-H bonds toward trifluoromethyl radical attack: at 164°, k_{CF_3}/k_{CH_3} is 8.0 (silane) and 100 (trimethylsilane). However, chlorination of silane has the opposite effect; the rate constant quotient for attack on trichlorosilane is reported as 0.4 and 1.2.

B. POSSIBLE ORIGINS OF REACTIVITY DIFFERENCES

Two different approaches have been made to explain the different reactivities of the two radicals, one involving enthalpy changes and the other involving polar effects and electronegativities. They are given in outline below.

1. *Enthalpy Differences*

For the reactions considered here

$$CF_3 + RH \longrightarrow CF_3H + R \qquad \Delta H_{CF_3}$$

$$CH_3 + RH \longrightarrow CH_4 + R \qquad \Delta H_{CH_3}$$

the difference in the enthalpies ($\Delta H_{CF_3} - \Delta H_{CH_3}$) is a reflection of the difference in dissociation energy of the bonds formed in the reactions, since the bond broken (R-H) is the same in both cases (see section III). We can thus write

$$(\Delta H_{CF_3} - \Delta H_{CH_3}) = D(CF_3\text{-}H) - D(CH_3\text{-}H)$$

Current values[76] for these bond strengths are $D(CF_3\text{-}H)$ = 106 kcal mol^{-1} and $D(CH_3\text{-}H)$ = 104 kcal mol^{-1}, whence ($\Delta H_{CF_3} - \Delta H_{CH_3}$) is about 2.0 kcal mol^{-1}. If this is reflected

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(175) H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **36**, 2196 (1962).

entirely in ($E_{CH_3} - E_{CF_3}$), then k_{CF_3}/k_{CH_3} would be *ca.* 10 at 164°.

However, empirical relationships such as that of Polanyi

$$E = \alpha \Delta H + \text{constant}$$

which applies to series of similar reactions,[174,176] show that only a fraction (α) of the enthalpy difference of 2 kcal mol^{-1} is reflected in the difference ($E_{CH_3} - E_{CF_3}$) since the constant α is always less than 1. Hence, it is improbable that the overall enthalpy difference alone could cause k_{CF_3}/k_{CH_3} to be greater than 5, say, at 164°.

This approach does not seem able to explain convincingly the increased reactivity of CF_3 over CH_3; it was put forward by Whittle as an alternative explanation to electronegativity differences between the two radicals in the light of his early measurements[134,177,178] of the CF_3–H bond strength. These early measurements indicated[179] that the bond energy difference ($D(CF_3\text{–}H) - D(CH_3\text{–}H)$) might be as large as 6 kcal mol^{-1}, whence it could be reasonably expected that ($E_{CH_3} - E_{CF_3}$) would be about 3 kcal mol^{-1}, the experimental value in many cases.

2. *Polar Effects*

Since fluorine is more electronegative than any other element, the CF_3 radical is strongly electrophilic, and this consideration has been put forward[19] to account for the enhanced reactivity of CF_3 toward CH bonds. Conversely, in attack on polar bonds, CF_3 radicals are not so favored because of repulsions from polar interactions; activation energies tend to be raised[180] relative to those for attack by methyl radicals.

Dipole–dipole repulsions are considered[161,172] to account for the pattern of reactivities found for the attack of methyl and trifluoromethyl radicals on hydrogen sulfide and the hydrogen halides. At 164°, the rate constant quotient (k_{CF_3}/k_{CH_3}) for attack on silane is 8.0; however, for attack on the Si–H bond in the more polar[181] trichlorosilane, the ratio is reduced to a value reported as 1.2 and 0.4. Cheng and Szwarc[182] have reported that, at 180°, for trifluoromethyl radical attack on $Si(CH_3)_4$, $ClSi(CH_3)_3$, $Cl_2Si(CH_3)_2$, and Cl_3SiCH_3, the CH bond reactivity decreased with successive substitution of methyl groups by chlorine atoms. Similar considerations can be used to explain the low values of k_{CF_3}/k_{CH_3} reported for attack on the fluoroalkyl formates.

Although Tedder[180] has considered that polar repulsions have little effect on methyl radical abstractions, Tarr, Coomber, and Whittle[183] have demonstrated that in the approximately thermoneutral series of reactions ($CH_3 + CH_4$, $CH_3 + H_2$, and $CH_3 + HCl$) the activation energy decreases by nearly 10 kcal mol^{-1}. The methyl radical is nucleophilic both in comparison with the CF_3 radical and in an absolute sense.[184]

In summary, the difference in reactivity between two radicals may be reasonably correlated with electronegativity differences, and the presence of polar repulsions between the attacking radical and certain groups in the substrate (mainly halogen and sulfur atoms) tends to favor CH_3 over CF_3 radicals. However, there seems to be no simple systematic trend between the activation energy difference ($E_{CH_3} - E_{CF_3}$) and the polarity of the substrate.[174,185]

XI. *Isotope Effects in Abstraction Reactions*

A. THEORETICAL CONSIDERATIONS

In the reactions considered here either a hydrogen atom or a deuterium atom is transferred according to the reactions

$$R + XH \longrightarrow RH + X \qquad (15)$$

$$R + XD \longrightarrow RD + X \qquad (16)$$

which proceed *via* the transition states $(R\text{–}H\text{–}X)^{\ddagger}$ and $(R\text{–}D\text{–}X)^{\ddagger}$, respectively.

From "classical" absolute rate theory[186,187] the ratio of rate constants, k_H/k_D, for reactions 15 and 16 is given by eq 17,

$$\frac{k_H}{k_D} = \left(\frac{M_H{}^{\ddagger}}{M_D{}^{\ddagger}}\frac{M_D}{M_H}\right)^{3/2}\left(\frac{A_H{}^{\ddagger}B_H{}^{\ddagger}C_H{}^{\ddagger}}{A_D{}^{\ddagger}B_D{}^{\ddagger}C_D{}^{\ddagger}}\frac{A_DB_DC_D}{A_HB_HC_H}\right)^{1/2} \times \prod_i^{3n-7}\frac{\sinh {}^1\!/_2U_i(D)}{\sinh {}^1\!/_2U_i(H)}\prod_i^{3n-6}\frac{\sinh {}^1\!/_2U_i(H)}{\sinh {}^1\!/_2U_i(D)} \qquad (17)$$

where M is the molecular mass, A, B, and C are the principal moments of inertia, and $U = h\nu/kt$. This general equation makes three principal assumptions: (i) that the transmission coefficients for the two isotopic reactions are the same, (ii) that the vibrations are simple harmonic, and (iii) that the transfer of the hydrogen atom can be treated by classical mechanics.

Generally, ratios of rate constants cannot be calculated from first principles, not only because little is known of the required parameters for the transition state but also because spectroscopic data for the reactant molecules are often incomplete. Therefore, in order to obtain numerical estimates it is necessary to make various approximations to eq 17 according to the isotope effect under investigation.

The simplest treatment of isotope effects involving hydrogen and deuterium assumes that, on passing from the reactants to the transition state, the zero-point energy associated with the stretching frequency of the bond attacked is lost. This is no arbitrary assumption but a fundamental tenet of the transition state theory which requires that one normal mode corresponds to a maximum in the energy surface. The frequency is thus imaginary and has no real zero-point energy.

Assuming also that the terms involving mass and moments of inertia in the general equation (17) can be equated to unity and that frequencies outside the reaction zone are unaffected in the transition state, the general equation reduces to

$$k_H/k_D = \exp(\Delta E_0/RT) \qquad (18)$$

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Table XXXVI

Isotope Effects for Methyl Radical Attack on NH and ND Bonds

Substrates	*Log* (A_H/A_D)	A_H/A_D	$E_D - E_H$, *kcal mol*$^{-1}$	k_H/k_D (*164°*)	*Ref*
NH_3, ND_3	−0.16 ± 0.65	0.69	1.1 ± 1.3	2.5 ± 0.8	153
$C_2H_5NH_2$, $C_2H_5ND_2$	−0.11 ± 0.50	0.78	1.1 ± 0.9	3.0 ± 0.6	97
CH_3NH_2, CH_3ND_2	−0.06 ± 0.27	0.87	1.3 ± 0.5	3.9 ± 0.4	25
$(NH_2CH_2)_2$, $(ND_2CH_2)_2$	−0.06 ± 0.18	0.87	1.1 ± 0.4	3.0 ± 0.4	78
$(CH_3)_2NH$, $(CH_3)_2ND$	0.16 ± 0.30	1.4	1.4 ± 0.7	7.2 ± 0.6	126
$(CH_2)_2NH$, $(CH_2)_2ND$	0.00 ± 0.14	1.0	1.7 ± 0.2	7.6 ± 0.6	101, 127
N_2H_4, N_2D_4	0.14 ± 0.18	1.4	1.4 ± 0.3	6.9 ± 0.6	89, 153
$(CH_3)_2NNH_2$, $(CH_3)_2NND_2$	−0.04 ± 0.23	0.91	1.1 ± 0.4	3.1 ± 0.3	89
CH_3ONH_2, CH_3OND_2	0.15 ± 0.19	1.4	1.4 ± 0.3	6.6 ± 0.6	107
$(CH_3NH)_2$, $(CH_3ND)_2$	−0.08 ± 0.26	0.83	0.8 ± 0.5	2.0 ± 0.3	89

where ΔE_0 is the difference in zero-point energy ($E_D - E_H$) for the stretching frequency of the bond attacked.

Since the zero-point energy is given by $E_0 = {}^1/_2h\nu = {}^1/_2hc\omega$, where ν is the vibrational frequency in sec^{-1} and ω is the wave number in cm^{-1}, whence $\Delta E_0 = {}^1/_2hc(\omega_H - \omega_D)$, where H and D refer to the bonds X-H and X-D. When hydrogen and deuterium are attached to a much heavier atom (as is often the case), it is a good approximation to write $(\omega_H/\omega_D) = 2^{1/2}$, so that ΔE_0 (erg) $= 0.146hc\omega_H$.

Values of ΔE_0, in kcal mol^{-1}, for various vibrational frequencies X-H from 2800 to 3800 cm^{-1} are given below[188] along with the predicted values of k_H/k_D at 164°.

ω, *cm*$^{-1}$	ΔE_0, *kcal mol*$^{-1}$	k_H/k_D *at 164°*
2800	1.17	3.8
3000	1.25	4.2
3200	1.34	4.7
3400	1.42	5.1
3600	1.50	5.6
3800	1.58	6.2

Equation 18 has the following consequences: (i) the ratio of A factors (A_H/A_D) should be equal to unity; (ii) the activation energy difference ($E_D - E_H$) should be equal to the appropriate difference in zero-point energies; (iii) values of k_H/k_D should remain reasonably constant in a series of similar substrates, since vibrational frequencies do not differ by much in such a series; (iv) the isotope effect should be independent of the attacking species. These points are examined in the light of available experimental data in the following section.

B. EXPERIMENTAL RESULTS

1. *Methyl Radical Attack*

The results available for the attack by methyl radicals on hydrogen and deuterium attached to nitrogen are given in Table XXXVI.

They illustrate the combination of experimental errors inherent in determinations of ratios of rate constants and Arrhenius parameters in gas-phase free radical reactions of this type. Errors attached to log (A_H/A_D) and ($E_D - E_H$) are derived by combination of standard deviations from least-mean-squares treatments and can thus be regarded as representing a 68% confidence limit. Errors attached to ratios of rate constants are estimated from the experimental scatter in the experimental results at 164°. Although subjective, they probably represent a confidence limit of about 90%. It is inherent in the procedures and emphasized by analysis of the errors that k_H/k_D is generally better known (at a particular, favorable temperature) than A_H/A_D or than $E_D - E_H$. As a consequence, much of the analysis of kinetic isotope effects must be based on the experimental velocity constant ratios.

It can be seen from the data presented in Table XXXVI that the first two predictions of the elementary treatment (eq 17) are statistically borne out by experiment. Within the admittedly large experimental error, the ratios of A factors (A_H/A_D) do not differ significantly from unity. Nor do the differences in activation energies ($E_D - E_H$) differ significantly from the difference in zero-point energies of 1.42 ± 0.04 calculated for a single N—H stretching vibration (the NH stretching frequency is taken[189] as 3400 ± 100 cm^{-1}).

The other predictions of the elementary treatment are that in such reactions values for k_H/k_D should be reasonably constant and equal, at 164°, to 5.1 with a possible deviation of about ±0.3. The data collected in Table XXXVI show these predictions are not fully borne out by experiment. Although the *average* value of 4.6 for k_H/k_D compares favorably with the predicted value, individual values spread from 2.0 ± 0.3 to 7.6 ± 0.6.

The results for methyl radical abstraction from C–H and C–D bonds are more plentiful and are presented in Table XXXVII. Errors in this table have been omitted partly for clarity of presentation but partly because many authors did not assess them. It is understood, however, that the errors attached to A_H/A_D are large although the values of k_H/k_D are more precise.

The first two predictions of the simple treatment are again borne out by the experimental results. With the exception of the results for methane and methyl acetate (see below), values for A_H/A_D lie close to unity and values for ($E_D - E_H$) do not differ significantly from the difference in zero-point energies of 1.21 ± 0.04 kcal mol^{-1} calculated for a single C–H stretching vibration (a value of 2900 ± 100 cm^{-1} is taken for a single C–H stretching vibration[189]).

As was the case for abstraction from N–H and N–D bonds, however, the other predictions based on the simple treatment are not borne out by experiment. At 164°, eq 17 predicts, for all substrates, a value for k_H/k_D of 4.0 ± 0.3, whereas most of the experimental values are greater. Excluding the anomalous isotope effects reported for methyl acetate and

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(188) Values given in R. P. Bell, "The Proton in Chemistry," Methuen, London, 1959, are corrected here.

(189) H. A. Szymanski, "Theory and Practice, I.R. Spectroscopy," Plenum Press, New York, N. Y., 1964, p 291.

Table XXXVII

Isotope Effects for Methyl Radical Attack on CH and CD Bonds

Substrates	A_H/A_D	$E_D - E_H$[a]	k_H/k_D (*164°*)	*Ref*
$\mathrm{CH_4, CD_4}$	0.17	3.1	6.2	91, 121
$\mathrm{C_2H_6, C_2D_6}$	1.0	1.5	5.6	90
$\mathrm{C_2H_6, CH_3CD_3}$	1.4	2.0	6.9	90
$\mathrm{CH_3CD_3, C_2D_6}$	0.51	1.4	5.1	90
$\mathrm{CH_3CD_3}$	0.71	1.9	6.3	90
$\mathrm{(CH_3)_2}\mathit{CH}_2\mathrm{, (CH_3)_2CD_2}$	1.0	1.4	5.1	90
$\mathrm{(CH_3}\mathit{CH}_2\mathrm{)_2, (CH_3CD_2)_2}$	0.62	2.1	6.9	90
$\mathrm{(CH_3)_3}\mathit{CH}\mathrm{, (CH_3)_3CD}$	0.80	1.6	5.0	90
$\mathrm{(CH_2)_6, (CD_2)_6}$	. . .	. . .	0.4	191
$\mathrm{C_6H_5}\mathit{CH}_3\ \mathrm{C_6H_5}\mathit{CD}_3$	1.0	1.8	7.9	95
$\mathit{CH}_3\mathrm{CONH_2, CD_3CONH_2}$	0.71	1.2	2.6	68
$\mathit{HC}\mathrm{ONH_2,}\ \mathit{DC}\mathrm{ONH_2}$	. . .	. . .	~6	67
$\mathit{CH}_3\mathrm{NH_2, CD_3NH_2}$	2.0	1.1	6.9	25
$\mathit{CH}_3\mathrm{OH, CD_3OH}$	0.89	1.9	7.8	66
$\mathit{CH}_3\mathrm{OH, CD_3OH}$	1.3	1.3	6.3	102
$\mathit{CH}_3\mathrm{OH, CD_3OH}$	1.6	1.2	6.3	103
$\mathrm{CH_3}\mathit{CH}_2\mathrm{OH, CH_3CD_2OH}$	0.98	1.7	6.9	112
$\mathrm{(CH_3)_2}\mathit{CH}\mathrm{OH, (CH_3)_2CDOH}$	0.78	1.8	6.0	66
$\mathit{H}\mathrm{CO_2CH_3, DCO_2CH_3}$	0.87	1.8	6.6	109
$\mathrm{CH_3COCH_3, CD_3COCD_3}$	0.69	1.9	6.2	112
$\mathrm{CH_3COCH_3, CD_3COCD_3}$	0.60	1.8	4.6	69
$\mathrm{CH_3COCH_3, CD_3COCD_3}$	0.85	1.6	5.8	90
$\mathrm{H_2CO, D_2CO}$	0.81	1.7	5.8	130
$\mathit{CH}_3\mathrm{COOCD_3, CD_3COOCH_3}$	0.46	5.6	290	110
$\mathrm{CD_3COO}\mathit{CH}_3\mathrm{, CH_3COO}\mathit{CD}_3$	0.58	0.19	0.72	110

[a] In kcal mol^{-1}.

Table XXXVIII

Isotope Effects for Methyl Radical Attack on OH, OD SH, and SD Bonds

Substrates	*Log* (A_H/A_D)	A_H/A_D	$E_D - E_H$, *kcal* mol^{-1}	k_H/k_D (*164°*)	*Ref*
$\mathrm{C_2H_5}\mathit{OH}\mathrm{, C_2H_5}\mathit{OD}$	0.11 ± 0.50	1.3	0.75 ± 1.0	3.1 ± 0.4	112
$\mathrm{H_2S, D_2S}$	−0.1	0.8	1.0	4.0	33, 69, 160

cyclohexane,[190] the average value of 6.0 is significantly higher than the predicted value. The values range from 2.6 to 7.9.

The extraordinary isotope effects reported for attack on methyl acetate (see Tables XXXVII and XL) throw serious doubts on the experimental findings. The system may have suffered interference by secondary reactions and we consider the results to be spurious (see also sections V, IX, and X).

Table XXXVIII presents data for the isotope effects arising from the abstraction of hydrogen and deuterium attached to oxygen and sulfur. Results are available only for ethanol and methyl mercaptan. For abstraction from O-H, at 164°, eq 17 becomes[192,193] $k_H/k_D = \exp(1.5\ \mathrm{kcal}/RT) = 5.8$. The experimental results for A_H/A_D and $E_D - E_H$ are consistent with the predicted values, but the experimental quotient $k_H/k_D = 3.1$ is significantly lower. For abstraction from hydrogen sulfide, the experimental results are in good agreement with the parameters (at 164°, $k_H/k_D = \exp(1.13\ \mathrm{kcal}/RT) = 3.7$) predicted by eq 17.

The results for methyl radical attack on H_2 and D_2 are presented in Table XXXIX. Using the frequencies 4395 and 3118 cm^{-1} for the vibrations in H_2 and D_2, at 164°, eq 17 becomes $k_H/k_D = \exp(1.84\ \mathrm{kcal}/RT) = 8.3$. All the experimental values for k_H/k_D are significantly lower and, at 164°, the average value is 4.0. Methyl radical abstraction of hydrogen and deuterium atoms from HD (Table XXXIX) presents a special case. In these reactions the same bond is broken, and thus on theoretical grounds the activation energies for abstraction of hydrogen atoms and deuterium atoms should be the same. However, because of large experimental errors attached to the experimental results, it is not possible to say whether this is so; values for $E_D - E_H$ of 0, 1.1, and 1.2 kcal mol^{-1} have been reported. The results do show, however, that, at 164°, the quotient k_H/k_D lies between 1.6 and 2.0. Whittle and Steacie[24] suggested that the experimental values for k_H/k_D can be explained by differences between the A factors arising from differences in the moments of inertia of the transition states $(CH_3\cdots H\cdots D)$ and $(CH_3\cdots D\cdots H)$. Their calculations showed that $I(CH_3\cdots H\cdots D)/I(CH_3\cdots D\cdots H)$ is 1.5 which agrees well with the experimental values of k_H/k_D (see also section IV).

2. *Trifluoromethyl Radical Attack*

The primary kinetic isotope effects for abstraction of hydrogen and deuterium atoms from CH bonds, by trifluoromethyl radicals, are presented in Table XL.

Table XXXIX

Isotope Effects for Methyl Radical Attack on H_2, D_2, and HD

Substrates	A_H/A_D	$E_D - E_H$, *kcal* mol^{-1}	k_H/k_D (*164°*)	*Ref*
H_2, D_2	0.6	1.7	4.5	21, 24, 80
H_2, D_2	1.6	0.7	3.7	24
H_2, D_2	2.0	0.7	3.7	21, 80
H_2, D_2	1	1.1	4.0	83
HD	0.4	1.3	2.0	24
HD	0.6	1.1	2.0	24[b]
HD[a]	1.6	0	1.6	24[c]

[a] The attacking radical is CD_3. [b] H and D rate parameters calculated from results of separate experiments. [c] H and D rate parameters calculated from results of same experiments.

The experimental values for A_H/A_D and $E_D - E_H$ do not, in general, differ (within the large experimental errors) from the values of $A_H/A_D = 1$ and $E_D - E_H = 1.2$ predicted by eq 17. Exceptions are the reported values for A_H/A_D of 6.3 and 0.02 for attack on methane[139] and methyl acetate.[110]

It is only when examining the more precise k_H/k_D values that we see significant divergencies from the value of 4.0 predicted

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[190] J. R. Majer and J. C. Robb, personal communication, have shown that the inverse isotope effect reported[191] for attack on cyclohexane and cyclohexane-d_6 was in error.

[191] J. R. Majer, W. D. Capey, and J. C. Robb, *Nature*, 203, 294 (1964).

[192] A. A. Herod, Ph.D. Dissertation, Leeds, 1967.

[193] C. E. Meloan, "Infrared Spectroscopy," Macmillan, New York, N. Y., 1963.

Table XL

Isotope Effects for Trifluoromethyl Radical Attack on CH and CD Bonds

Substrates	A_H/A_D	$E_D - E_H$[b]	k_H/k_D (*164°*)	*Ref*
CH_4, CD_4	6.3	1.1	25	139
CH_4, CD_4	1.3	1.7	9.2	140
CHD_3	0.51[a]	2.3	6.9[a]	148
$\mathit{CH}Cl_3$, $CDCl_3$	1.6	2.7	32	139
CH_3NH_2, CD_3NH_2	0.49	1.9	4.2	51
CH_3OH, CD_3OH	0.4	2.3	5.6	143
CH_3OH, CD_3OH	0.63	1.9	5.8	50
$\mathit{H}CO_2CH_3$, DCO_2CH_3	1.0	1.8	8.7	109
CH_3COOCD_3, CD_3COOCH_3	0.91	3.6	57	110
$CD_3\ COO\mathit{CH}_3$, $CH_3COO\mathit{CD}_3$	0.02	3.7	1.02	110

[a] On a per atom basis. [b] In kcal mol^{-1}.

by the simple treatment. All the experimental values of k_H/k_D are greater than 4.0, and they range from 4.2 to the spectacularly high values of 25, 32, and 57 reported for attack on methane,[139] trichloromethane,[139] and methyl acetate.[110]

Experimental results for trifluoromethyl radical abstraction of hydrogen and deuterium from ammonia,[156] dimethylamine,[52] hydrogen chloride, and hydrogen sulfide[162] are grouped together in Table XLI. For attack on the two nitrogen compounds the predicted values are $A_H/A_D = 1$, $E_D - E_H = 1.4$, and k_H/k_D at 164° = 5.0. The experimental values for A_H/A_D and $E_D - E_H$ do not differ significantly from the predicted ones. The value for k_H/k_D of 4.1 reported for attack on ammonia is possibly in satisfactory agreement, but the value of 2.0 reported for attack on dimethylamine is significantly lower than the predicted one.

Table XLI

Isotope Effects for Trifluoromethyl Radical Attack on Other Bonds

Substrates	A_H/A_D	$E_D - E_H$, *kcal mol*$^{-1}$	k_H/k_D (*164°*)	*Ref*
NH_3, ND_3	1.2	1.1	4.1	156
$(CH_3)_2\mathit{NH}$, $(CH_3)_2\mathit{ND}$	0.39	1.4	2.0	52
HCl, DCl	0.93	0.73	2.3	162
H_2S, D_2S	0.81	0.74	1.5	162

For attack on HCl and D_2S the parameters predicted by the simple treatment are the same, *viz.* $A_H/A_D = 1$, $E_D - E_H = 1.13$ kcal mol^{-1}, and k_H/k_D at 164° = 3.7. Again, the experimental values for the Arrhenius parameters do not differ significantly from those predicted. However, both experimental determinations of k_H/k_D are significantly lower.

The experimental results for the isotope effects arising from the trifluoromethyl radical attack on the hydrogen isotopes are given in Table XLII. For attack on H_2 and D_2,[19,87,88] the results can be compared with those predicted by the simple treatment: $A_H/A_D = 1$, $E_D - E_H = 1.84$ kcal mol^{-1}, and k_H/k_D at 164° = 8.3. Neither the values for A_H/A_D nor those for $E_D - E_H$ appear to differ significantly from the predicted values. The quotients k_H/k_D are, however, lower by a factor of *ca.* 2 than that predicted.

Table XLII

Isotope Effects for Trifluoromethyl Radical Attack on H_2, D_2, and HD

Substrates	A_H/A_D	$E_D - E_H$, *kcal mol*$^{-1}$	k_H/k_D (*164°*)	*Ref*
H_2, D_2	2.6	0.7	5.0	88
H_2, D_2	1.4	0.86	4.0	19
H_2, D_2	1.3	1.1	4.3	87
HD	0.78	0.86	1.3	87
HD	2.4	0.3	1.6	88

The results for attack on HD[87,88] are consistent with the interpretation that the isotope effect arises from a difference between the moments of inertia for the respective transition states (see section 1 above).

C. DISCUSSION

1. Rough Classification of Isotope Effects

The results presented above show that, although the simple treatment is fairly useful in predicting ratios of *A* factors and differences in zero-point energies, it is unable to predict many of the observed values of k_H/k_D. Unfortunately since a rigorous treatment based on eq 15 demands detailed specification of the transition state, about which our knowledge is minimal, we can only discuss qualitatively the factors which can cause the observed variations in values of k_H/k_D. We have arbitrarily taken the value predicted by the simple treatment as a norm and classified k_H/k_D values as "high" and "low." Those values obtained for methyl radical abstraction are given in Table XLIII. The assignment of values as high or low was made, where possible, by assessing the error attached to k_H/k_D and taking as significant a difference of more than three times the standard deviation between the experimental value and the "norm."

For abstraction from C–H bonds k_H/k_D values tend to be "high." Fourteen out of the 17 abstractions studied led to decidedly high values, while only two can be classified as low. High, low, and normal values for k_H/k_D are found for abstraction from NH bonds (five "low" values lie between 2.0 and 3.1 while three "high" values lie between 6.9 and 7.6). The results obtained for abstraction from OH and SH bonds and the results for hydrogen are low.

It is of interest, especially since the simple treatment predicts that isotope effects are independent of attacking species, to compare this classification for methyl attack with a similar one for attack by trifluoromethyl radicals. Although there are fewer results available for abstraction by trifluoromethyl radicals, it can be seen from Table XLIV that a similar pattern emerges. Isotope effects for abstraction from C–H bonds are generally "high" while those for attack on other bonds are generally "low."

A comparison of individual reactions shows that for attack on methane, the methyl group in methanol, and the formyl hydrogen in methyl formate, high values of k_H/k_D are obtained for both methyl and trifluoromethyl attack. For attack on the methyl group in methylamine, a high isotope effect is found for attack by methyl radicals and a normal one for attack by trifluoromethyl radicals. For abstraction from NH bonds, dimethylamine and ammonia behave quite differently toward methyl and trifluoromethyl radical attack. Thus for methyl attack on dimethylamine the isotope effect is high (7.2), while

Table XLIII

Classification of Isotope Effects (k_H/k_D at 164°) for Methyl Radical Abstractions

"Low" values	*"Normal" values*	*"High" values*
	C–H Bonds	
$[(\mathrm{C}\mathit{H}_2)_6$ (0.4)]?	$(\mathrm{CH_3})_3\mathrm{C}\mathit{H}$ (5.0)	$\mathrm{CH_4}$ (6.2)
$\mathrm{C}\mathit{H}_3\mathrm{CONH_2}$ (2.6)		$\mathrm{C_2H_6}$ (5.6, 6.9, 5.1, 6.3)
$\mathrm{CD_3COOC}\mathit{H}_3$ (0.72)		$\mathit{H}\mathrm{CONH_2}$ (∼6)
		$(\mathrm{CH_3})_2\mathrm{C}\mathit{H}_2$ (5.1)
		$(\mathrm{CH_3C}\mathit{H}_2)_2$ (6.9)
		$\mathrm{C}\mathit{H}_3\mathrm{NH_2}$ (6.9)
		$\mathrm{C}\mathit{H}_3\mathrm{OH}$ (7.8, 6.3, 6.3)
		$\mathrm{CH_3C}\mathit{H}_2\mathrm{OH}$ (6.9)
		$(\mathrm{CH_3})_2\ \mathrm{C}\mathit{H}\mathrm{OH}$ (5.9)
		$\mathrm{HCO_2CH_3}$ (6.6)
		$\mathrm{C}\mathit{H}_3\mathrm{COC}\mathit{H}_3$ (6.2, 5.8, 4.6)
		$\mathrm{C_6H_5C}\mathit{H}_3$ (7.9)
		$\mathit{H}_2\mathrm{CO}$ (5.8)
		$\mathrm{C}\mathit{H}_3\mathrm{COOCH_3}$ (288)
	N–H Bonds	
$(\mathrm{CH_3N}\mathit{H})_2$ (2.0)	$\mathrm{CH_3N}\mathit{H}_2$ (3.9)	$(\mathrm{CH_2})_2\mathrm{N}\mathit{H}$ (7.6)
$\mathrm{NH_3}$ (2.5)	$\mathrm{CH_3ON}\mathit{H}_2$ (6.6)	$(\mathrm{CH_3})_2\mathrm{N}\mathit{H}$ (7.2)
$\mathrm{C_2H_5N}\mathit{H}_2$ (3.0)		$\mathrm{N_2H_4}$ (6.9)
$(\mathrm{N}\mathit{H}_2\mathrm{CH_2})_2$ (3.0)		
$(\mathrm{CH_3})_2\mathrm{NNH_2}$ (3.1)		
	O–H Bonds	
$\mathrm{C_2H_5O}\mathit{H}$ (3.1)		
	Other Bonds	
$\mathrm{H_2}$ (4.5, 3.7, 3.7, 4.0)		
	$\mathrm{H_2S}$ (4.0)	

Table XLIV

Classification of Isotope Effects (Quotients of Velocity Constants at 164°) for Trifluoromethyl Radical Reactions

"Low" values	*"Normal" values*	*"High" values*
	C–H Bonds	
$\mathrm{CH_3COOC}\mathit{H}_3$ (1.02)	$\mathrm{CH_3NH_2}$ (4.2)	$\mathrm{CH_4}$ (9.2, 25, 6.9)
		$\mathrm{CHCl_3}$ (32)
		$\mathrm{C}\mathit{H}_3\mathrm{OH}$ (5.6, 5.8)
		$\mathit{H}\mathrm{CO_2CH_3}$ (8.7)
		$\mathrm{C}\mathit{H}_3\mathrm{COOCH_3}$ (57)
	N–H Bonds	
$(\mathrm{CH_3})_2\mathrm{N}\mathit{H}$ (2.0)	$\mathrm{NH_3}$ (4.1)	
	Other Bonds	
HCl (2.3)		
$\mathrm{H_2S}$ (1.5)		
$\mathrm{H_2}$ (5.0, 4.0, 4.3)		

for attack by CF_3 it is "low" (2.0). The opposite trend is shown by ammonia.

A comparison of the isotope effects for methyl and trifluoromethyl radical attack on hydrogen sulfide reveals that for methyl attack the isotope effect is "normal" but for trifluoromethyl radical attack it is "low" (1.5).

Attack on H_2 and D_2 by both attacking radicals produce "low" isotope effects, and there appears to be little significant difference between the two sets of results.

2. *Interpretation of "Low" Isotope Effects in Terms of Transition State Vibrations*

Low isotope effects have been explained in terms of transition state vibrations, the frequencies of which are affected by the substitution of deuterium for hydrogen.

Westheimer[194] pointed out that if the transition state can be regarded as a linear triatomic species it will involve the following normal modes of vibration

$$\overset{\leftarrow}{\mathrm{A}}\text{——}\overset{\rightarrow}{\mathrm{H}}\text{——}\overset{\leftarrow}{\mathrm{B}} \qquad \nu_1$$

$$\overset{\leftarrow}{\mathrm{A}}\text{——}\overset{?}{\mathrm{H}}\text{——}\overset{\rightarrow}{\mathrm{B}} \qquad \nu_2$$

$$\overset{\uparrow}{\mathrm{A}}\text{——}\underset{\downarrow}{\mathrm{H}}\text{——}\overset{\uparrow}{\mathrm{B}} \qquad (\nu_3 \text{ doubly degenerate})$$

The unsymmetrical stretching vibration ν_1 is the vibration corresponding to the reaction coordinate and according to transition state theory is imaginary and should thus be denoted $i\nu_1$. Because it is not a real vibration and can therefore have no real zero-point energy, it must be discounted as a source of mass-dependent zero-point energy in the transition state. The "symmetrical" stretching vibration ν_2 can, however, involve considerable movement of the central atom and thus become a source of mass-dependent zero-point energy in the transition state. This vibration will involve motion of the central atom only when the triatomic species is unsymmetrical. If the complex is symmetrical (*i.e.*, the masses of A and B are equal and force constants k_{A-H} and k_{B-H} are equal), then the center of gravity of the complex rests at the central atom which remains stationary during the vibration.

If the isotope effect is influenced by this vibration, then it follows that in a series of similar compounds the isotope effect will be a maximum when the transition state (R–H–X) is symmetrical. This is tested by reference to the data present here.

A difference in mass between R and X would explain on these grounds the "low" isotope effects found for both CH_3 and CF_3 attack on hydrogen, since the force constants in the transition states would be expected to be similar.

The low value obtained for the methyl radical attack on the OH bond in ethanol can also be rationalized in terms of the symmetric vibration. The transition state will be asymmetrical and force constants representing R–H and X–H would be expected to be quite different. Similar observations can be made in the systems where CF_3 radicals attack hydrogen chloride and hydrogen sulfide.

Three of the "low" values found for methyl attack on NH bonds [$(CH_3)_2NNH_2$, $(NH_2CH_2)_2$, $(CH_3NH)_2$] involve transition states that are highly asymmetric, and this gives some support to the theory. However, the appearance of the NH_3 system in this category is most surprising since the transition state ($CH_3\cdots H\cdots NH_2$) should be highly symmetrical, the force constants for $CH_3\cdots H$ and $NH_2\cdots H$ would be expected to be similar (the bond dissociation energies $D(CH_3\text{–}H)$ and $D(NH_2\text{–}H)$ differ only by 1 or 2 kcal mol^{-1}), and the masses of CH_3 and NH_2 are identical.

It can be seen that for abstraction from C–H bonds by methyl and trifluoromethyl radicals there is no correlation with this prediction. Systems involving both symmetric (CH_4, C_2H_6) and highly unsymmetrical transition states (such as $(\mathrm{CH_3C}\mathit{H}_2)_2$ or $(\mathrm{CH_3})_2\mathrm{C}\mathit{H}\mathrm{OH}$)) have k_H/k_D values which are

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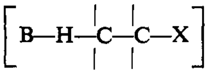
(194) S. H. Westheimer, *Chem. Rev.*, 61, 265 (1961).

all randomly high. In addition, the low isotope effect found for attack on acetamide will also involve a highly unsymmetrical transition state. Thus, although in some cases it is possible to see some correlation between low k_H/k_D values and the symmetry of the three-center transition state, it is clear that this explanation is far from satisfactory.

Bell[195] has taken this treatment further by considering the transition state as a linear five-atom complex to describe, in particular, such reactions as base catalyzed β eliminations which proceed *via* an E2 "concerted" mechanism. Bell considers that these reactions proceed through a transition state which is represented as



$$\left[\mathrm{B{-}H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X}\right]$$

where B is the attacking base and X is the eliminated group.

Such a transition state will have four stretching modes which can be presented by

$$\underset{\text{i}}{\mathrm{\vec{B}{-}\overset{\leftarrow}{H}{-}\vec{C}{-}\overset{\leftarrow}{C}{-}\vec{X}}} \qquad \underset{\text{ii}}{\mathrm{\overset{\leftarrow}{B}{-}\overset{?}{H}{-}\vec{C}{-}\overset{\leftarrow}{C}{-}\vec{X}}}$$

$$\underset{\text{iii}}{\mathrm{\vec{B}{-}\overset{\leftarrow}{H}{-}\overset{?}{C}{-}\vec{C}{-}\vec{X}}} \qquad \underset{\text{iv}}{\mathrm{\overset{\leftarrow}{B}{-}\overset{\leftarrow}{H}{-}\overset{?}{C}{-}\vec{C}{-}\vec{X}}}$$

Mode i represents the reaction coordinate and will thus have no real zero-point energy. Mode ii is the analog of the symmetric vibration of the three-center transition state, and mode iv will probably be of low frequency and not very dependent on the hydrogen mass. The interesting vibration is that represented by mode iii. In this vibration the B-HC part of the vibration resembles the reaction coordinate except that the vibration will be highly dependent on the mass of the hydrogen even when it is symmetrically placed in the transition state.

The conclusion[195] of this treatment is that the concerted nature of the mechanism leads to a real vibration unsymmetrical as far as the B-H-C system is concerned, and therefore permits large variations in the magnitude of the isotope effect.

It is not necessary to the above arguments that the mechanism leads to the concerted cleavage of the bond. It could equally well apply to mechanisms in which there is a concerted change in bond length or bond angle. The low isotope effect reported for abstraction from the methyl group in acetamide (at 164°, $k_H/k_D = 2.6$) could be explained as involving in the transition state a concerted change in the C-O bond length. In this case the mode iii vibration is represented as

$$\mathrm{\overset{\rightarrow}{Me}{-}\overset{\leftarrow}{H}{-}\overset{?}{C}{-}\vec{C}{-}\vec{O}}$$

Similar considerations could provide explanations of other observed low isotope effects.

Other vibrations in the transition state that have been held responsible for low isotope effects are the doubly degenerate bending vibrations of the three-center transition state. Although the frequencies of these vibrations are expected to be lower than the stretching vibrations, they will contribute double and could therefore be a source of mass-dependent zero-point energy in the transition state. Although there is no direct measurement of the magnitude of these frequencies, they are quite likely to be of the same order of magnitude as the C-H bending frequency in isobutane (1400 cm^{-1}) or the bending frequency of the HF_2 ion (1225 cm^{-1}). These frequencies will decrease as the bond is stretched, but they may still be present in the transition state. Their effect will be to decrease the isotope effect.

3. *Interpretation of "High" Isotope Effects in Terms of Transition State Vibrations*

High isotope effects have been explained by loss of bending vibrations in the transition state[196] and by quantum mechanical tunneling. In this section we outline the explanation in terms of transition state vibrations; tunneling is considered in section 4 below.

The high isotope effects are explained by making the assumption that in the transition state the bond attacked is stretched to such an extent that the doubly degenerate X-H bending frequencies approach zero. With the usual assumptions the general equation (17) then reduces to the form

$$k_H/k_D = \frac{1}{2}\exp\left\{\frac{1}{2}\sum_{1}^{3}[U_i(\mathrm{H}) - U_i(\mathrm{D})]\right\} \qquad (19)$$

This treatment thus predicts values of A_H/A_D equal to 0.5 and values of $E_D - E_H$ equal to the appropriate difference in zero-point energies. However, as before, no conclusions—as far as A_H/A_D and $E_D - E_H$ values are concerned—can be drawn because of the large errors attached to these parameters. Because of the lower uncertainty, k_H/k_D values are examined below.

Substituting values for the C-H stretching (2900 cm^{-1}) and C-H bending (1400 cm^{-1}) vibrations and the corresponding C-D frequencies obtained using the expression $\omega_H/\omega_D = 2^{1/2}$, eq 19 becomes

$$k_H/k_D = 0.5\exp(2.38\ \mathrm{kcal}/RT) \qquad (20)$$

At 164°, k_H/k_D is equal to 7.8 which is to be compared with a value of 4.0 obtained by the simple treatment (eq 18).

It must be borne in mind that the frequencies used above are only average values (with an uncertainty of about ± 100 cm^{-1}) and that the corresponding frequencies for C-D vibrations are obtained using an approximation. Use of experimental frequencies can lead to values for k_H/k_D different from the value found above since small deviations from the average can become significant when summing over three vibrations. For example, substituting experimental values of vibration frequencies for the CH_4-CD_4 system (CH and CD stretches are 3020 and 2258, and CH and CD bendings are 1306 and 996 cm^{-1}, respectively), eq 19 becomes

$$k_H/k_D = 0.5\exp(1.98\ \mathrm{kcal}/RT)$$

which at 164° reduces to $k_H/k_D = 4.9$, a significantly lower value than the general value of 7.8 obtained above. However, it can be seen that the effect of this treatment is to increase the predicted value nearer to the values obtained experimentally (see Table XXXVII) where an average value of 6.0 (at 164°) is found.

This treatment, however, does not explain so well the high isotope effects found for attack at NH and N-D bonds. Taking the bending frequency for N-H as 739 cm^{-1} (the inversion frequency), application of eq 19 leads to the expression

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[195] R. P. Bell, *Discuss. Faraday Soc.*, 39, 16 (1965).

[196] M. Salomon, *Can. J. Chem.*, 42, 610 (1964).

$$k_H/k_D = 0.5 \exp(2.02 \text{ kcal}/RT)$$

which, at 164°, gives a value for $k_H/k_D = 5.1$.

This value is, in fact, only slightly higher than the corresponding value of 5.0 predicted by the simple treatment. It appears, therefore, that this treatment can provide no explanation of the high isotope effects for abstraction of hydrogen and deuterium attached to nitrogen, and this must cast some doubt on its application generally.

4. *Quantum Mechanical Tunneling*

The contribution of quantum mechanical tunneling must, strictly, be taken into account in any treatment of isotope effects involving hydrogen atoms, and its effect will always be to enlarge the value of k_H/k_D. However, it is clear from the occurrence of "low" isotope effects that in many cases the effect of tunneling is more than nullified by other factors. The issue under discussion here is not whether quantum mechanical tunneling is occurring but whether or not the high isotope effects measured are caused by *large* contributions from tunneling.

Besides leading to large k_H/k_D ratios, contributions from tunneling would be expected to show themselves in two other ways. First, values of A_H/A_D may be found less than 0.5, which is the lower limit in the absence of tunneling, and, secondly, values for $E_D - E_H$ may occur that exceed the appropriate difference in zero-point energies. In general, the results do not reveal these effects though it is apparent, from the large errors attached to $E_D - E_H$ and A_H/A_D, that only spectacularly large contributions from quantum mechanical tunneling would result in statistically significant deviations.

Johnston and Rapp[197] have performed calculations, based on transition state models, and by invoking quantum mechanical tunneling have obtained good agreement with experiment for the methyl radical attack on hydrocarbons. Only the results for methyl radical attack on methane and methane-d_4, however, reveal the Arrhenius parameters ($A_H/A_D = 0.17$ and $E_D - E_H = 3.1$ kcal mol^{-1}) one would expect from a significant tunneling contribution. There are only two results which, if valid, require explanation by quantum mechanical tunneling. The first is for the trifluoromethyl radical attack on methane and methane-d_4 for which a value of 25 has been reported[139] for k_H/k_D at 164°. The second is for the trifluoromethyl radical attack on trichloromethane and trichloromethane-d_1, where at 164° (k_H/k_D) was reported as 32. For both these studies, however, there are serious doubts about the experimental findings. A later study[140] of the trifluoromethyl radical attack on methane and methane-d_4 led to an isotope effect, at 164°, of only 9.2, and since the attack of methyl radical on trichloromethane led to interference by secondary reactions involving chlorine atoms, it is possible that the same interference was present in the study of attack by trifluoromethyl radicals.

XII. Appendices

A. APPENDIX I. REACTION RATE PARAMETERS FOR ETHYL AND PERFLUOROETHYL RADICAL ABSTRACTIONS

This section is included to present a brief outline of the data available for hydrogen and deuterium atom abstraction by C_2H_5 and C_2F_5 radicals. We have restricted our discussion to unambiguous reactions, and it is intended to compare the behavior of the ethyl radical with the perfluoroethyl radical and to draw parallels with the work on CH_3 and CF_3 radicals.

1. *Ethyl Radical Attack*

The principal data are listed in Table XLV. Of the results for attack on hydrogen,[198-201] the recent work[199,200] is probably the most reliable. At 164°, k is $10^{5.8}$ cm^3 mol^{-1} sec^{-1} and E is *ca.* 14.0 kcal mol^{-1}. Since the difference in bond energies ($D(CH_3\text{-}H) - D(C_2H_5\text{-}H)$) is *ca.* 6 kcal mol^{-1}, it is to be expected that attack by ethyl radicals will be less favored than attack by methyl radicals (see section X). For H_2, where CH_3 attack is approximately thermoneutral and C_2H_5 attack is endothermic, the activation energy for C_2H_5 attack (*ca.* 14 kcal mol^{-1}) is greater than that for CH_3 attack (*ca.* 12 kcal mol^{-1}) and the order of reactivities is as expected.

The rate parameters for the dimerization of ethyl radicals (commonly used as the reference reaction) are not firmly established. It has been customary to assume[202,203] a value for the rate constant of $10^{14.0}$ cm^3 mol^{-1} sec^{-1}. However, the experimental parameters[204] of $A = 10^{14.5}$ cm^3 mol^{-1} sec^{-1} and $E = 2$ kcal mol^{-1} have been used,[199] and a recent review[1] uses a value of $k = 10^{13.4}$ cm^3 mol^{-1} sec^{-1}, following Benson.[205] This latter value will be employed here.

For abstraction of hydrogen from neopentane[206] and cyclohexane,[198] at 164°, the ethyl radical is less reactive than the methyl by a factor of between 6 and 24. For cyclohexane, the A factors are approximately the same for attack by both radicals and the difference in reactivity originates in the greater activation energy for ethyl radical attack (E (kcal mol^{-1}) = 10.4 (C_2H_5) and *ca.* 8.7 (CH_3)). For attack on neopentane, the A factors are different by a factor 10 while the activation energies are different by only 0.6 kcal mol^{-1}, both differences favoring methyl radical attack.

For ethyl radical attack on diethyl ketone[202,206-211] different investigators have reported values for the rate constant at 164°, close to $k = 10^{7.2}$ cm^3 mol^{-1} sec^{-1}. Only one investigation employed isotopic labeling, that for the attack of CH_3CD_2 radicals on diethyl-d_4 ketone. At 164°, deuterium is abstracted from the α position eight times as fast as is hydrogen from the β position. Thus, in the substrates $(CH_3CH_2)_2CO$ and $(CD_3CD_2)_2CO$ attack is predominantly at the α position. The Arrhenius parameters for deuterium abstraction from diethyl-d_4 ketone have been revised[211] to give a rate constant,

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[198] P. J. Boddy and E. W. R. Steacie, *Can. J. Chem.*, **39**, 13 (1961).

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Table XLV

Hydrogen and Deuterium Abstraction Reactions of Ethyl Radicals

Substrate	*Radical source*[a]	*Temp range, °C*	*E, kcal mol^{-1}*	*Log A (cm^3 mol^{-1} sec^{-1})*	*Log k*[b] *(cm^3 mol^{-1} sec^{-1})*	*Ref*
H_2	ket-d_{10}	50–300	11.3	11.50	5.85	198
H_2	prop oxid	440	14.10	12.81	5.76	199
H_2	$Hg(^3P_1) + C_2H_4 + H_2$	240–320	13.70	12.57	5.72	200
D_2	ketone	54–286	13.3	12.22	5.57	201
D_2	prop oxid	440	14.70	12.61	5.25	199
neo-C_5H_{12}	ket-d_{10}	50–300	12.6	11.25	4.95	206
c-C_6H_{12}	ket-d_{10}	50–300	10.4	11.42	6.22	198
$(C_2H_5)_2CO$	ket	90–160	7.80	11.1	7.2	202
$(C_2H_5)_2CO$	ket	50–215	7.80	11.1	7.2	207
$(C_2H_5)_2CO$	ket	40–160	7.6	11.0	7.2	208
$(C_2H_5)_2CO$	ket	15–170	8.9	11.7	7.3	209
$(\mathit{CH}_3\mathrm{CD}_2)_2\mathrm{CO}$	ket-d_4	25–365	11.7	11.4	5.6	210
$(\mathrm{CH}_3\mathit{CD}_2)_2\mathrm{CO}$	ket-d_4	25–365	8.7	10.8	6.5	210
$(\mathrm{CH}_3\mathit{CD}_2)_2\mathrm{CO}$	ket-d_4	25–365	9.2	11.1	6.5	210, 211
$(C_2D_5)_2CO$	ket-d_{10}	25–314	9.6	11.3	6.6	211
$(C_2D_5)_2CO$	ket-d_{10}	50–300	9.0	11.0	6.5	206
$C_2F_5COC_2H_5$	$C_2F_5COC_2H_5$	100–250	6.8	10.8	7.4	212
$(C_2H_5)_2N_2$	azo	27–175	8.0	11.5	7.5	213
$(C_2H_5)_2N_2$	azo	74–178	7.5	10.9	7.2	214
N_2H_4	ket	90–157	4.6	10.4	8.1	202
$(CH_3)_3N$	ket	90–158	7.4	10.1	6.4	202
HI	C_2H_5I/IH	263–300	1.1	11.9	11.4	215

[a] ket = diethyl ketone; ket-d_{10} = perdeuteriodiethyl ketone; azo = azoethane; prop oxid = proprionaldehyde oxidation. [b] At 164°.

at 164°, of $10^{6.5}$ cm^3 mol^{-1} sec^{-1}, an activation energy of 9.2 kcal mol^{-1}, and an A factor of $10^{11.1}$ cm^3 mol^{-1} sec^{-1}. These parameters are indistinguishable from the parameters for C_2D_5 attack on diethyl-d_{10} ketone[211] where k, at 164°, is $10^{6.6}$ cm^3 mol^{-1} sec^{-1}, E = 9.6 kcal mol^{-1}, and $A = 10^{11.3}$ cm^3 mol^{-1} sec^{-1}. The kinetic isotope effect for attack at the α position in diethyl ketone is $k_H/k_D = 5.0$, $E_D - E_H = 1.4$ kcal mol^{-1}, and $A_H/A_D = 1.0$, in agreement with isotope effects shown by methyl radical reactions with CH bonds (see section XI).

Within rather wide limits of error, azoethane and diethyl ketone have similar reactivities toward ethyl radical attack. This contrasts with the results for methyl radical attack on azomethane and acetone where attack on azomethane, at 164°, was found to be more reactive by a factor of 2.5. Ethyl radical attack on hydrogen iodide is rapid (at 164°, $k = 10^{11.4}$ cm^3 mol^{-1} sec^{-1}). The corresponding attack by methyl radicals is three times faster, at 164°, as a consequence of a larger A factor: the activation energy for both reactions is about 1.2 kcal mol^{-1}.

Similarly, at 164°, the ethyl radical attack on tetramethylsilane and trichlorosilane is slower than the corresponding attack by methyl radicals, though a result in both reactions[165,167] of activation energies higher by ~1 kcal mol^{-1}.

A comparison of rate parameters for the ethyl and methyl radical attack on trimethylamine shows that attack by methyl radicals, at 164°, is faster by a factor of 10. However, the superior reactivity originates in the difference in A factors (A (cm^3 mol^{-1} sec^{-1}) = $10^{11.4}$ (methyl) and $10^{10.1}$ (ethyl)) since the activation energy for attack by methyl radicals is greater by 1.3 kcal mol^{-1}. An identical situation exists for attack on hydrazine where the greater reactivity toward methyl attack, at 164° ($k_{CH_3}/k_{C_2H_5} = 2.5$) is again due to a superior A factor (A (cm^3 mol^{-1} sec^{-1}) = $10^{11.0}$ (methyl) and $10^{10.4}$ (ethyl)) as the activation energy for attack by methyl is somewhat greater (E (kcal mol^{-1}) = 5.0 (methyl) and 4.6 (ethyl)).

It thus appears from the limited number of comparisons available that the ethyl radical is less reactive than the methyl radical in hydrogen abstraction reactions although the reactivity difference seems to depend on both activation energy and A-factor differences.

2. Perfluoroethyl Radical Attack

The available results are listed in Table XLVI. As the rate constant for the reference reaction (the dimerization of perfluoroethyl radicals) has not been measured but assumed to be $10^{14.0}$ cm^3 mol^{-1} sec^{-1}, individual rate constants could be in error by a factor of 2 (or more).

The C_2F_5–H bond strength is given as 103 kcal mol^{-1}, which is some 3 kcal mol^{-1} less than the CF_3–H bond strength. This implies that the C_2F_5 radical should be marginally less reactive than the CF_3 radical. Both radicals are polar and strongly electronegative.

The reactions of perfluoroethyl radicals with H_2 and D_2 are endothermic by 1 or 2 kcal mol^{-1} which is reflected in a larger activation energy[13,216,217] than that observed for attack by trifluoromethyl radicals. For H_2,[13] E (kcal mol^{-1}) is 8.8, 9.5, or 10.7 for attack by CF_3 and 11.9 and 12.4 for attack by C_2F_5.

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Table XLVI

Hydrogen and Deuterium Atom Abstraction Reactions of Perfluoroethyl Radicals

Substrate	*Radical source*[a]	*Temp range, °C*	*E, kcal mol*$^{-1}$	*Log A (cm*^{3} *mol*$^{-1}$ *sec*$^{-1}$*)*	*Log k*[b] *(cm*^{3} *mol*$^{-1}$ *sec*$^{-1}$*)*	*Ref*
H_2	ket	137–237	11.9	12.72	6.77	13
H_2	C_2F_5CHO	157–319	12.4	13.20	7.00	216
D_2	C_2F_5CHO	146–313	12.6	12.45	6.15	216
D_2	azo	153–258	14.1	13.08	6.03	217
CH_4	ket	150–272	10.6	11.62	6.32	13
C_2H_6	azo	84–226	8.70	12.18	7.83	217
c-C_6H_{12}	azo	28–132	6.0	12.18	9.18	217
CF_3CHO	azo	138–220	9.70	12.40	7.55	217
C_2F_5CHO	C_2F_5CHO	150–310	4.90	10.74	8.29	216
C_2F_5CHO	C_2F_5CHO	27–307	4.50	10.49	8.24	218
CH_3COCH_3	azo	82–219	8.40	11.71	7.51	217
$C_2F_5COC_2H_5$	ket	50–250	5.6	11.34	8.54	212

[a] ket = perfluorodiethyl ketone; azo = perfluoroazoethane. [b] At 164°.

However, because of the higher *A* factor for attack by perfluoroethyl radicals, the rate constants at 164° are not significantly different.

At 164°, perfluoroethyl radical attack on ethane[217] is faster than on methane by a factor of 32 owing to a lowering in activation energy of 1.9 kcal mol^{-1}. The results for attack on cyclohexane[217] show that abstraction is rapid (*k*, at 164°, is $10^{9.2}$ cm^3 mol^{-1} sec^{-1}) owing to a low activation energy of 6.0 kcal mol^{-1}.

When compared with the corresponding trifluoromethyl reactions (see section V), the results show that for methane,[13] ethane,[217] and cyclohexane,[217] the rate constants, at 164°, are the same (within probable experimental error) whether the attacking radical is CF_3 or C_2F_5. Similarly, the attack on acetone[217] by the two radicals proceeds with similar rate constants and Arrhenius parameters. For attack on the CH bonds in the fluoroalkyl aldehydes, at 164°, CF_3CHO[217] is equally reactive toward perfluoroethyl and trifluoromethyl radicals while C_2F_5CHO[216,218] is more reactive toward perfluoroas a result of an activation energy difference of 1.7 kcal mol^{-1}.

From this brief discussion it would appear that the perfluoroethyl and trifluoromethyl radicals show similar reactivities toward hydrogen and CH bonds.

3. Comparisons of C_2H_5 and C_2F_5

It is to be expected on thermochemical ground that C_2F_5 radicals will be more reactive than C_2H_5 radicals for attack on the same substrate ($D(C_2F_5\text{–}H) - D(C_2H_5\text{–}H)$ = *ca.* 5 kcal mol^{-1}). It is also reasonable to conjecture that differences between CH_3 and CF_3 radicals might be paralleled by differences between C_2H_5 and C_2F_5 radicals. Few substrates common to all radicals have been studied.

The data indicate that, as expected, C_2F_5 radicals are more reactive toward hydrogen and deuterium than are C_2H_5 radicals. For attack on hydrogen, at 164°, ($k_{C_2F_5}/k_{C_2H_5}$) is *ca.* 10 which can be compared with the value of *ca.* 2.5 obtained for the corresponding attack by CF_3 and CH_3 radicals. For attack on cyclohexane, at 164°, $k_{C_2F_5}/k_{C_2H_5}$ is *ca.* 900 (the corresponding ratio k_{CF_3}/k_{CH_3} is *ca.* 60). A somewhat lower value ($k_{C_2F_5}/k_{C_2H_5} = 12$) is obtained for abstraction from the more polar substrate $C_2F_5COC_2H_5$, and interest centers on possible quotients for the substrates hydrogen iodide and hydrogen sulfide where, at 164°, attack by CH_3 was found to be faster than attack by CF_3 radicals.

B. APPENDIX II. SELECTED BOND DISSOCIATION ENERGIES

It is the purpose of this section to present bond dissociation energies to which reference has been made in this review. Unless stated otherwise they are taken from the values compiled by Kerr.[76] In addition, we have included comment on some bond energies about which there is uncertainty where the kinetic data presented here have thrown light on their possible values.

1. C–H Bond Dissociation Energies

The following values, in kcal mol^{-1}, have been used: $D(CH_3\text{–}H) = 104 \pm 1$, $D(C_2H_5\text{–}H) = 98 \pm 1$, $D(CH_3CH_2CH_2\text{–}H) = 98 \pm 2$, $D((CH_3)_3CCH_2\text{–}H) = 99.3 \pm 1$, $D((CH_3)_2CH\text{–}H) = 94.5 \pm 1$, $D(CH_3CH_2CH(CH_3)\text{–}H) = 94.6 \pm 1$, $D((CH_3)_3C\text{–}H) = 91.0 \pm 1$, $D(C_6H_5CH_2\text{–}H) = 85 \pm 1$, $D(c\text{-}C_3H_5\text{–}H) = 101 \pm 3$, $D(c\text{-}C_4H_7\text{–}H) = 95 \pm 3$, $D(c\text{-}C_5H_9\text{–}H) = 93.3 \pm 1$, $D(c\text{-}C_6H_{11}\text{–}H) = 94 \pm 3$, $D(c\text{-}C_7H_{13}\text{–}H) = 93 \pm 3$, $D(CF_3\text{–}H) = 106 \pm 1$, $D(CF_2H\text{–}H) = 101 \pm 4$, $D(H\text{–}CH_2F) = 101 \pm 4$, $D(C_2F_5\text{–}H) = 103 \pm 2$, $D(CCl_3\text{–}H) = 95.7 \pm 1$, $D(H\text{–}OH) = 119 \pm 1$, $D(H\text{–}CH_2OH) = 92 \pm 2$, $D(H\text{–}CH_2OCH_3)$[219] $= 92.9$, $D(CH_3COCH_2\text{–}H) = 92 \pm 3$, $D(H\text{–}CHO) = 88 \pm 2$, $D(CH_3CH(OH)\text{–}H) = 90 \pm 2$, $D(CH_3CO\text{–}H) = 88 \pm 2$.

a. $D(C_6H_5\text{–}H)$

For a number of years a value around 104 kcal mol^{-1} has been accepted[76] but a value of 112 kcal mol^{-1} has been recently reported.[131] Results for the system $CH_3 + C_6H_6$ are capable of resolving this conflict since the higher value would make the reaction some 8 kcal endothermic and little hydrogen abstraction would be expected. Despite the fact that Krech and Price[9] detected and measured rates for the abstraction process, we believe their results may be spurious (see section V) and would favor the higher value of 112 kcal mol^{-1}.

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b. $D(H-CH_2NH_2)$

No experimental value exists for this parameter but an estimate can be obtained from comparison with the isoelectronic analogs ethane and methanol. The bond dissociation energies, $D(H-CH_2CH_3)$ and $D(H-CH_2OH)$ are 98 ± 1 and 92 ± 2 kcal mol^{-1} and activation energies (kcal mol^{-1}) for attack by methyl radicals (see Table III) are *ca.* 11.7 (ethane) and 10.0 (methanol). Since the activation energy for attack on methylamine has been reported as 8.7 and 9.0 kcal mol^{-1}, a bond dissociation energy of $D(H-CH_2NH_2) = 88 \pm 2$ kcal mol^{-1}, somewhat lower than that found in methanol, is to be expected.

2. N–H Bond Dissociation Energies

The following values, in kcal mol^{-1}, have been used: $D(CH_3NH-H) = 92 \pm 3$, $D((CH_3)_2N-H) = 86 \pm 3$, $D(H-N_3)$[220] $= 90 \pm 8$.

a. $D(NH_2-H)$

The bond dissociation energy for $D(NH_2-H)$ is dependent on the value for $\Delta H_f(NH_2)$. Values for $\Delta H_f(NH_2)$ have been derived from kinetic decomposition studies of hydrazine, and a value of 56 ± 2 kcal for $D(NH_2-NH_2)$ is listed by Kerr.[76] We believe, however, that in view of the scattered values reported[221] for $D(NH_2-NH_2)$ the error limits would be better described as ±6. We have adopted $D(NH_2-H) = 102.5 \pm 3$, and regard this as a lower limit.

b. $D(C_2H_5NH-H)$ and $D(NH_2CH_2CH_2NH-H)$

There is no experimental value for $D(C_2H_5NH-H)$ but in view of the similar reactivity of the NH_2 groups in methylamine and ethylamine toward attack by methyl radicals (see section VI), a bond dissociation energy close to that for methylamine is indicated. In addition, the close resemblance between ethylamine and ethylenediamine both in their reactivity toward radical attack and in the molecular environment of the NH_2 groups suggests that $D(C_2H_5N-H)$ and $D(NH_2CH_2CH_2NH-H)$ can both be estimated as 92 ± 3 kcal mol^{-1}.

c. $D(N_2H_3-H)$

The activation energy of 5 kcal mol^{-1} for the methyl radical abstraction of hydrogen atoms from hydrazine suggests a lower bond dissociation energy than that of 102.5 ± 3 found for ammonia, where methyl radical attack produced an activation energy of 10 kcal mol^{-1}. A very much lower mass spectrometric value of 75 ± 5 kcal mol^{-1} has been reported[222] although the drop below ammonia seems too large. A value of *ca.* 93 kcal mol^{-1}, supported by a comparison[153] with bond strengths in the isoelectronic ethane and hydrogen peroxide, appears more reasonable.

d. $D(H-NCO)$

The inertness of isocyanic acid toward attack by methyl radicals (section VI) indicates a bond dissociation energy greater than the C–H bond in methane. On this basis, $D(H-NCO) > 104$ kcal mol^{-1}.

3. O–H and S–H Bond Dissociation Energies

The following values, in kcal mol^{-1}, have been used: $D(HO-H) = 119 \pm 1$, $D(CH_3O-H) = 102 \pm 2$, $D(C_2H_5O-H) = 102 \pm 2$, $D(HS-H) = 90 \pm 2$, $D(CH_3S-H) = 88$.

C. APPENDIX III. REACTION RATE PARAMETERS FOR SOME REVERSE REACTIONS

In this appendix, data are presented for free radical attack on methane, some experimental but mostly calculated from the kinetic data in this review. The Arrhenius parameters will be compared in the light of the thermochemistry of the reactions and of family relationships among the attacking species.

Where direct kinetic data for radical attack on methane are lacking, they can often be obtained from experimental measurements on the kinetics of the reverse reactions provided there is adequate knowledge of the thermodynamics of the overall reaction. As was outlined in section III, the Arrhenius parameters for the foward and reverse reactions are related by the equations

$$\log (A_f/A_r) = \Delta S^\circ/2.303R$$

$$E_f - E_r = \Delta H^\circ = D(CH_3-H) - D(X-H)$$

where the subscripts f and r denote forward and reverse reactions.

Since there are values for many bond dissociation energies, values for E_f can be obtained for many reactions where E_r is experimentally known. Such bond energy data are listed in Appendix II.

Experimental values for the entropy change often do not exist, but sufficiently reliable entropy values can be calculated from first principles or estimated from semiempirical methods with a basis in statistical mechanics. Since, for most free radicals, the moments of inertia and vibrational frequencies are not known, the second alternative has been employed here. The method is that devised by Benson and Buss.[223] This is based on statistical theory in the manner in which the contributions of electron degeneracy and symmetry are incorporated and uses the results of experiment for estimating a self-consistent set of group-entropy terms. The principles may be expressed by the equation

$$S^\circ = R \ln(\text{electronic degeneracy}) - R \ln(\text{symmetry number}) + \Sigma(\text{atomic contributions})$$

In this expression, the symmetry number (σ) is defined as the number of indistinguishable positions that can be obtained by rotation of the species as a whole and by internal rotations. The electronic degeneracy (g) is unity for a molecule with all its electrons paired, and is equal to 2 for a radical with one unpaired electron.

Table XLVII presents the entropy values calculated using this method (and also indicates where necessary the shape of the species assumed in computing the symmetry number, σ).

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Table XLVII

Entropies of Radicals and Molecules Derived from Atomic Contributions

$$S^\circ = R \ln g - R \ln \sigma + \Sigma(\text{atomic entropy terms})$$

Species	*Shape assumed*	*Σ(entropy terms)*	*σ*	*S°*[a]	*Exptl value*	*Ref*
CH_3	Nonplanar	49.5	3	48.7		
CH_4		51.4	12	46.5	44.5	224
OH		46.5	1	49.4	45.1	225
H_2O		50.8	2	49.4	45.1	225
NH_2	Bent	47.8	2	47.8		
NH_3		50.9	3	48.7	46.0	225
CH_3NH	Bent	57.2	3	56.4		
CH_3NH_2		60.3	3	58.1	57.7	225
CH_2NH_2	Nonplanar	58.4	1	59.8		
$(CH_3)_2N$	Bent	66.6	18	62.3		
$(CH_3)_2NH$		69.7	9	65.3	63.5	225
$(CH_3)_2NNH$		75.5	9	72.5		
$(CH_3)_2NNH_2$		78.6	9	74.2		
CH_3NHNCH_3		75.5	9	72.5		
$(CH_3NH)_2$	Cis	78.6	9	74.6		
N_2H_3		56.7	1	58.1		
N_2H_4		59.8	1	59.8		
C_2H_5NH	Bent	66.6	3	65.8		
C_2H_5NH		69.7	3	67.5	68.5	225
$(CH_2)_2N$		24.6	2	24.6		
$(CH_2)_2NH$	Nonplanar	27.7	1	27.7		
CH_3CHNH_2	Nonplanar	67.7	3	66.9		
$(NH_2CH_2)_2$		78.6	1	78.6		
$NH_2CHCH_2NH_2$		76.7	1	78.1		
$NH(CH_2)_2NH_2$		75.5	1	76.9		
HS		48.0	1	49.4		
H_2S		54.8	2	53.4	49.2	225
C_2H_5		58.9	3	58.1		
C_2H_6		60.8	18	55.7	54.9	224
$(CH_3)_2CH$		68.3	9	65.3		
$(CH_3)_2CH_2$		70.2	18	64.5	64.5	224
$(CH_3)_3C$		77.7	81	70.9		
$(CH_3)_3CH$		79.6	81	71.0		
$CH_3CH_2CH_2$		68.3	3	67.5		
n-C_3H_8		70.2	18	64.5	64.5	224
$CH_3CH_2CH_2CH_2$		77.7	3	76.9		
n-C_4H_{10}		79.6	18	73.9	74.1	224
CH_3O		55.9	3	55.1		
CH_2OH	Nonplanar	57.6	1	59.0		
CH_3OH		59.5	3	57.3	57.3	223, 226
C_2H_5O		65.3	3	64.5		
CH_3CHOH	Nonplanar	67.6	3	66.8		
C_2H_5OH		69.5	3	67.3	67.5	226
$(CH_3)_2CHO$		74.7	9	71.7		
$(CH_3)_2COH$		74.1	9	71.1		
$(CH_3)_2CHOH$		76.0	9	71.6	74.1	227
CH_3OCH_3		69.4	18	63.7	63.7	226
CH_2OCH_3		67.5	3	66.7		
$CH_3CHOC_2H_5$		87.5	9	84.5		
$C_2H_5OC_2H_5$		89.4	18	83.7		
$(CH_3)_2COC_3H_7$		100.5	81	93.7		
$(i$-$C_3H_7)_2O$		102.4	162	92.3		
CH_3S		57.4	3	56.6		
CH_3SH		64.2	3	62.0	60.9	226
CF_3		63.0	3	62.2	60.7	162, 228
CF_3H		64.9	3	62.7	62.0	228

[a] At 25°.

Where experimental values[223–228] are available, they are included for comparison. It is important to note that differences between individual experimental and calculated values (which are typically 2 cal deg^{-1} mol^{-1}) usually lead only to small uncertainty in A_t. The reasons are that (i) errors tend to cancel because of the symmetry of the reactions considered here and (ii) $\Delta S°$ values obtained for hydrogen abstraction are subject to far smaller uncertainties than $\Delta S°$ values for decompositions and associations. We are here concerned with reactions (about 36 in number) in which methane is subjected to attack by different atoms and radicals. Interest centers on (1) family relationships among the attacking species and (2) the kinetic influences of the strengths of the X–H bonds being formed; the bond being broken is always the same.

1. *Attack by Halogen Atoms*

The data for the reactions in which methane is attacked by the halogens F, Cl, Br, and I show that while the A factors do not indicate any significant change, the activation energies decrease with decreasing atomic weight of the halogens. As would be expected, these decreases in activation energy parallel the changes in the exothermicity of the reaction and hence the increases in the strength of the bond formed in the reaction. The trend, however, is not smooth. As one passes from I to Br or from Br to Cl an increase of 15 kcal mol^{-1} in the strength of the bond being formed is accompanied by an equal decrease (kcal mol^{-1}) in activation energy; from Cl to F a further increase of 32 kcal mol^{-1} in bond strength results in a decrease of only 2.6 kcal mol^{-1} in E. One common factor is that for the exothermic reactions ($F + CH_4, CH_3 + HCl$, HBr and HI) the activation energies are constant at 1.2 kcal mol^{-1}. The transition states are presumably identical in each case.

A similar pattern is formed in the Arrhenius parameters for the reactions of halogen atoms with hydrogen molecules ($X + H_2 = XH + H$):

Attack on H_2	*F*	*Cl*	*Br*	
Log A, cm^3 mol^{-1} sec^{-1}	13.8	13.3 or 13.9	14.1	14.4
E, kcal mol^{-1}	1.7	5.5	19.7	34.1

The variations in the preexponential factors are again not significant, but the activation energies exhibit the same, somewhat irregular, trend with D(H–X) as do those for attack on methane. The similarities between the activation energies for attack on hydrogen (above) and on methane (E (kcal mol^{-1}) = 1.2, 3.8, 18.5, and *ca.* 34 for F, Cl, Br, and I) may be correlated with the identical thermochemistry of these reactions, which, in turn, arises because $D(CH_3–H)$ and D(H–H) are both close to 104 kcal mol^{-1}.

In the case of hydrogen atom attack on methane[79] or H_2[1,229] the activation energies lie in between those for attack by chlorine and bromine atoms (for $H + CH_4$, E = 11.9 kcal mol^{-1} and for $H + H_2$, E is between 7 and 8 kcal mol^{-1}).

2. *Attack by Members of Isoelectronic Groups of Radicals*

a. CH_3, NH_2, OH, and F

An examination of the kinetic data for the reactions in which methane is attacked by the members of this family shows no clear pattern in A factors (they lie between $10^{11.3}$ and $10^{14.1}$ cm^3 mol^{-1} sec^{-1}) but a regular trend in activation energies: 14.7 for CH_3, 11.5 for NH_2, 5.0 for OH, and 1.2 for F. This parallels the trend in exothermicities (0, +1.5, −15, and −20), the strengths of the bonds formed (104, 102.5, 119, and 134 kcal mol^{-1}), and the electronegativities of the attacking radicals, although on these figures a somewhat higher activation energy for attack by NH_2 than the value found might have been expected.

b. Thiyl and Chlorine

Arrhenius parameters for attack on methane by SH and Cl show the same relation as those for their lower homologs OH and F. The A factors in cm^3 mol^{-1} sec^{-1} (A(SH) = $10^{12.8}$ and A(Cl) = $10^{13.4}$) do not differ much, but the activation energies in kcal mol^{-1} (E(SH) = 16.9 and E(Cl) = 3.8) display very conspicuously the consequences of the 12 kcal mol^{-1} difference between the strengths D(H–Cl) = 102 and D(H–SH) = 90 kcal mol^{-1} of the bonds formed in the two cases.

The same thermochemical factor governs the relationship between OH and SH. Abstraction by SH is much slower than abstraction by OH, an effect similar to that found above for attack by fluorine and chlorine atoms. The superior reactivity of the hydroxyl attack is due partly to a higher A factor (A (cm^3 mol^{-1} sec^{-1}) = $10^{13.5}$ compared with $10^{12.8}$ for attack by SH) but mainly due to a much lower activation energy (5.0 kcal mol^{-1} compared with 16.9 for attack by SH). This large difference in activation energies is in accord with the thermochemistry of these reactions, the bond strength in H_2O being greater by 29 kcal mol^{-1} than the bond strength in H_2S.

c. Ethyl, Methylamino, and Methoxyl

The bond strengths reported for the hydrogen derivatives are $D(C_2H_5–H)$ = 98, $D(CH_3NH–H)$ = *ca.* 92, and $D(CH_3O–H)$ = 102. The measured (at 164°) velocity constants for attack on methane do show minimum reactivity for methylamino, but no systematic pattern can be found in the Arrhenius parameters. The A factors are $10^{11.7}$, $10^{10.5}$, and $10^{11.6}$ cm^3 mol^{-1} sec^{-1} and the activation energies 17.7, 17.7, and 11.0, kcal mol^{-1} for C_2H_5, CH_3NH, and CH_3O, respectively.

d. *n*-Propyl, Ethylamino, and Ethoxyl

These three radicals show no definite trend in activation energy; E (kcal mol^{-1}) is 17.5 for *n*-propyl, 18.5 for ethylamino, and 11.4 for ethoxyl. The A factors are $10^{11.4}$, $10^{10.8}$, and $10^{12.0}$, respectively, and show no regular trend.

e. Ethyl, Aminomethyl, and Hydroxymethyl

The A factors are all similar and in the range $10^{11.4-11.7}$. The activation energy for the hydroxy radical is 22.0 kcal mol^{-1} and that for the aminomethyl radical is 18 kcal mol^{-1}, not significantly different from that for ethyl (17.7 kcal mol^{-1}).

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(224) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," API Project 44, Carnegie Press, Pittsburgh, Pa., 1952.

(225) "Selected Values of Thermodynamic Properties," Circular 500, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1952.

(226) J. H. S. Green, *Quart. Rev., Chem. Soc.*, 15, 125 (1961).

(227) J. H. S. Green, *Trans. Faraday Soc.*, 59, 1559 (1963).

(228) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1962.

(229) D. J. LeRoy, B. A. Ridley, and K. A. Quicket, *Discuss. Faraday Soc.*, 44, 92 (1967), and references therein.

f. Isopropyl, 1-Aminoethyl, and 1-Hydroxyethyl

The activation energies are all about the same (19.6, 19.1, and 19.7 kcal mol^{-1}, respectively) and the *A* factors are similar for isopropyl and 1-aminomethyl with that for 1-hydroxyethyl a factor of 3 greater.

g. Isobutyl, 2-Aminoisopropyl, and 2-Hydroxyisopropyl

No data are available for the 2-aminoisopropyl radical, but from the previous two reactions all three radicals might be expected to have the same activation energies. The activation energies for isobutyl and 2-hydroxyisopropyl are the same (21 kcal mol^{-1}), and the increase over those above reflects the increasing endothermicity of the reactions. The two *A* factors are the same ($10^{11.9}$ cm^3 mol^{-1} sec^{-1}) and not significantly different from those of the radicals CH_2X and CH_3CHX.

From these figures it seems clear that substitution of CH_3 by NH_2 or OH in a radical has little effect on the behavior of the radical toward methane.

3. *Attack by Members of Homologous Series*

a. Alkyl Radicals

Table XLVIII presents the kinetic and thermochemical data for the attack on methane by the radicals CH_3, C_2H_5, $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2$, $(CH_3)_2CH$, and $(CH_3)_3C$. A most striking feature is the closeness of the *A* factors which vary only from $10^{11.3}$ to $10^{11.9}$ cm^3 mol^{-1} sec^{-1}. Although there is no regular variation in activation energy as the homologous series is ascended (*i.e.*, in the series CH_3, C_2H_5, C_3H_7, etc.), the activation energies exhibit an almost regular increase with the endothermicity of the reaction.

b. Substituted Alkyl Radicals

These radicals are the series CH_2X, CH_3CHX, and $(CH_3)_2CX$ where X is CH_3, NH_2, and OH. The *A* factors (cm^3 mol^{-1} sec^{-1}) for all these radicals lie between $10^{11.3}$ and $10^{11.9}$ except for 1-hydroxyethyl, where *A* is $10^{12.2}$. The activation energies follow the same trend in each series with *E* going from about 18 kcal mol^{-1} in CH_2X to about 19.5 kcal mol^{-1} in the CH_3CHX radicals and to 21 kcal mol^{-1} in $(CH_3)_2CX$ radicals. The series of alkoxyalkyl radicals, CH_2OCH_3, $CH_3CHOC_2H_5$, and *i*-$C_3H_7OC(CH_3)_2$, follow much the same pattern as the hydroxyalkyl radicals. Likewise, the 1,2-diaminoethyl radical fits in well with the aminomethyl and 1-aminoethyl radicals in activation energy (18.3 kcal mol^{-1}) and *A* factor ($10^{11.5}$ cm^3 mol^{-1} sec^{-1}).

c. Amino Radicals

A similar state of affairs to that above is found when comparing the kinetic data for the attack on methane of the amino radicals NH_2, CH_3NH, C_2H_5NH, $(CH_2)_2N$, N_2H_3, $(CH_3)_2NNH$, and CH_3NHCH_3N. Although our theoretical knowledge of these reactions leans heavily on calculated data, the activation energies show an almost regular increase with the endothermicity of the reaction similar to that found for attack by hydrocarbon radicals. However, the *A* factors for these reactions vary over a much wider range ($10^{10.5}$ to $10^{12.2}$ cm^3 mol^{-1} sec^{-1}) than do the *A* factors for attack by hydrocarbon radicals.

Table XLVIII

Arrhenius Parameters for Hydrogen Abstraction from Methane

Radical	*Source*[a]	*Log A (cm^3 mol^{-1} sec^{-1})*	*E, kcal mol^{-1}*	*ΔH, kcal mol^{-1}*	*D(R–H), kcal mol^{-1}*	*Ref*
H	f	14.1	11.9	0	104	79
F	f	14.1	1.2	−20	134	1
Cl	f	13.4	3.8	2	102	1
Br	f	13.8	18.2	17	87	1
I	f	14.7	34.1	33	71	1
	f	14.9	35.0	33	71	1
	r	14.7	33.5	33	71	1
OH	f	13.5	5.0	−15	119	157
OCH_3	r	11.5	11.5	2	102	192
OCH_3	r	11.6	11.0	2	102	103
OC_2H_5	r	12.0	11.4	2	102	192
SH	r	12.8	16.9	14	90	159, 33
SCH_3	r	12.6	20.1	16	88	69
NH_2	r	11.5	11.8	15	102.5	230
NHC_2H_5	r	10.8	18.5	12	92	230
N_2H_3	r	11.9	16.0	11	93	230
$NHCH_3$	r	10.5	17.7	12	92	230
$NH(CH_2)_2NH_2$	r	11.5	18.3	11	92	192
$N(CH_3)_2$	r	11.9	23.4	17	~87	230
$N(CH_2)_2$	r	11.4	22.6	17	~87	230
$(CH_3)_2NNH$	r	12.2	23.8	18	~86	230
CH_3NHCH_3N	r	10.8	25.1	23	~81	230
CH_3	f	11.8	14.7	0	104	91
	f	11.3	14.2	0	104	90
$CH_3CH_2CH_2CH_2$	r	11.4	17.6	6	~98	90
C_2H_5	r	11.7	17.7	6	98	90
$CH_3CH_2CH_2$	r	11.4	17.5	6	98	90
$(CH_3)_2CH$	r	11.7	19.6	10	95	90
$(CH_3)_3C$	r	11.9	21.0	13	91	90
CH_2OH	r	11.4	22.0	12	92	192
CH_3CHOH	r	12.2	19.7	10	~94	192
$(CH_3)_2COH$	r	11.8	20.9	13	~91	192
CH_2OCH_3	r	11.4	21.0	11	93	192
$CH_3CHOC_2H_5$	r	12.3	19.7	10	~94	192
$(CH_3)_2COC_3H_7$	r	11.3	20.9	13	~91	192
CF_3	f	11.9	11.0	−2	106	1
CH_2NH_2	r	11.3	18.0	9	~95	153
$NH_2CHCH_2NH_2$	r	11.5	18.3	11	~93	192
CH_3CHNH_2	r	11.7	19.1	11	~93	89

[a] f, direct experimental determination; r, evaluated from reverse reaction.

d. Alkoxyl Radicals

Experimental data for the radicals OH, OCH_3, and OC_2H_5 can be compared; the experimental work[192] on methyl radical attack on isopropyl alcohol is complicated by secondary reactions, and the parameters obtained are not meaningful. The increase in activation energy in going from OH (5.0 kcal mol^{-1}) to CH_3O and C_2H_5O (each about 11.4 kcal mol^{-1}) is to be expected in view of the difference in bond strengths (17 kcal mol^{-1}) between HO–H and CH_3O–H. The *A* factors for CH_3O and C_2H_5O radicals are less than for OH radical attack by a factor of 10^3. The parameters for CF_3 attack on methane

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(230) P. Gray and A. Jones, *Can. J. Chem.*, 45, 333 (1967).

are included in Table XLVIII; these Arrhenius parameters are almost identical with those for alkoxyl radical attack.

e. Thiyl Radicals

Lack of data again limits comparisons to the Arrhenius parameters for attack by the first two members, SH and SCH_3. The data of Table XLVIII are in accord with expectations. The *A* factors ($cm^3\ mol^{-1}\ sec^{-1}$) of the two reactions are essentially equal ($10^{12.8}$ and $10^{12.6}$, respectively) and the corresponding activation energies of 16.9 and 20.1 kcal mol^{-1} reflect a decrease in the SH bond strength in H_2S and CH_3SH of *ca.* 2 kcal mol^{-1}.