REACTIONS OF RADICALS CONTAINING FLUORINE

A Thesis submitted for the degree of
DOCTOR OF PHILOSOPHY
of the University of Edinburgh

by

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Department of Chemistry,
University of Edinburgh. 1st October 1969.
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PREFACE

The research described in this thesis was carried out by the author in the Department of Chemistry of the University of Edinburgh, under the supervision of Dr. J.C.J. Thynne, between October 1966 and October 1969, is claimed as original, and has not been submitted for a degree elsewhere; with the following exceptions.

a) Methyl radical attack on trifluoroacetaldehyde was investigated in partial fulfilment of the requirements for the degree of B.Sc., with honours in chemistry, in this University.

b) Much of the experimental work on methyl radical attack on perfluoropropionaldehyde and perfluorobutyraldehyde was carried out by Mr. N.C. Beaton, the author having been responsible for the construction and maintenance of the apparatus, preparation of the aldehydes, and partial supervision of the research project.

Department of Chemistry,
University of Edinburgh. 1st October 1969.
DEDICATION

To my Mother.
ACKNOWLEDGEMENTS

Thanks are due to Professor Kemball for the provision of library and laboratory facilities, to the technical staff of this department, in particular Mr. Colin Baxter, Mr. John Broom and Mr. Alan King, whose advice and assistance proved invaluable on many occasions, to Professor Ebsworth and Dr. Gradock for guidance in the preparation of silanes, and to the occupants, past and present, of Rooms 130 and 144 who, throughout the last three years, have contributed so much, in terms of both ideas and practical assistance.

I am deeply grateful to Dr. John Thynne, whose drive and infectious enthusiasm have been a source of constant encouragement throughout the course of this research. It is a privilege to have worked under his guidance.
**ABSTRACT**

The following Arrhenius parameters for hydrogen (or deuterium) atom abstraction have been measured.

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<th>Log A</th>
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\( E \) is in kcal/mole, \( A \) in mole\(^{-1}\)cm\(^3\)sec\(^{-1}\)

In cases of ambiguity, the hydrogen or deuterium atom abstracted is underlined. Where the substrate is in brackets, the Arrhenius parameters refer to overall abstraction.

(Error Limits \( ± 1 \) Standard Deviation)

TFMI \( \sim \) trifluoromethyl iodide HFA \( \sim \) hexafluoroacetone

DTBP \( \sim \) di-tertiary-butyl peroxide AZO \( \sim \) azomethane

A value of 1.95 \( ± \) 0.07, which is independent of temperature, has been obtained for the cross-combination ratio of the radicals \( \text{CF}_3^\cdot \) and \( \text{C}_2\text{F}_5^\cdot \).

Butene formed during the photolysis of HFA in the presence of n-butane is attributed to the disproportionation reaction

\[
\text{C}_4\text{H}_9^\cdot + \text{CF}_3^\cdot \rightarrow \text{C}_4\text{H}_8 + \text{CF}_3\text{H}
\]

Similar reactions of other alkyl and perfluoroalkyl radicals are discussed. Inhibition of olefin formation (and consequently of formation of fluoroform other than by abstraction)
when TFMI is used as radical source, is explained in terms of the removal of alkyl radicals by reactions of the type
\[
R^* + I \rightarrow RI
\]
\[
R^* + I_2 \rightarrow RI + I^*.
\]

The importance of the reaction
\[
R_fCHO + h\nu \rightarrow R_fH + CO
\]
in the photolysis of perfluoroaldehydes is discussed, and has been shown by photolysing \(R_fCHO\) in the presence of nitric oxide.

The formation of perfluoroethane and fluoroform during the photolysis of TFMI/Ammonia mixtures cannot be explained solely by the reactions
\[
CF_3^* + CF_3^* \rightarrow C_2F_6
\]
and \[
CF_3^* + NH_3 \rightarrow CF_3H + NH_2^*.
\]

Rate constants for \(CF_3^*\) attack on polar molecules are interpreted in terms of dipole-dipole interactions between the radical and the substrate molecule. Activation energies measured for hydrogen atom abstraction by \(CF_3^*\) were found to fall below those for \(CH_3^*\) by amounts close to 3 kcal/mole.
Substitution of atoms of fluorine for those of hydrogen may have profound effects on the physical and chemical behaviour of a substance. In the last thirty years considerable industrial and scientific interest has been aroused by the electrical properties and chemical inertia of materials such as PTFE. Fluorocarbon analogues of most of the homologous series of organic compounds have been prepared, and the study of their reactions represents a major area of chemical research. The object of the present work is to extend our knowledge of the reactions of perfluoroalkyl radicals, and to compare their behaviour with that of alkyl radicals. Where the necessary data for comparison have not been reported the corresponding alkyl radical reactions have also been studied.

Reactions of free radicals occur in such a way as to reduce the instability generally associated with their possession of an unpaired electron. The principal modes of reaction are outlined below.

**COMBINATION:**

\[ R' + R'' \rightarrow RR' \]

The rate of such a reaction is governed by two factors: the third-body requirement which, at pressures above a few cm., is significant only for combination of atoms, and steric effects, most marked in the case of complex radicals.

**DISPROPORTIONATION:**

\[ \text{e.g. } \text{C}_2\text{H}_5^* + \text{C}_2\text{H}_5^- \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 \]
The activation energies for both combination and disproportionation reactions are generally taken to be zero, although some workers have reported slight positive values. It follows that the disproportionation/combination ratio is independent of temperature. (e.g. For ethyl radicals the rate of formation of ethylene, $R\text{C}_2\text{H}_4 = 0.13 \text{R}_\text{C}_4\text{H}_{10}$.)

**ADDICTION:**
\[ R' + A = B \rightarrow RAB' \]

Free radicals will readily add to an unsaturated molecule to form a larger radical.

**DECOMPOSITION:**
\[ RAB' \rightarrow R' + A = B \]

Radicals can decompose to produce an unsaturated molecule and a smaller radical.

**ISOMERISATION:**

The stability of many of the larger free radicals may be increased by the migration of atoms or groups of atoms.

**e.g.** $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}^\cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \tag{1}$

**TRANSFER REACTIONS:**

\[ R' + R'X \rightarrow RX + R' \]

a) **DISPLACEMENT:** Here the radical $R'$ takes the place of an atom or group in a molecule.

b) **ABSTRACTION:** The species abstracted, $X$, may be an atom or group. The distinction between group displacement and group abstraction is not clear-cut, but depends
on the relative sizes of $R'$ and $X$. e.g. The reaction

$$\text{CF}_3' + \text{CD}_3\text{OH} \rightarrow \text{CF}_3\text{OH} + \text{CD}_3'$$

encountered in this work, could be regarded as abstraction of a hydroxyl group, or displacement of a trideuteromethyl group, by a trifluoromethyl radical.

While no investigation of isomerisation or decomposition of organo-fluorine radicals has been described, the other modes of reaction mentioned above have been the subject of a considerable amount of research, which is summarised after the following brief discussion of available radical sources.

RADICAL SOURCES

Trifluoromethyl radicals may be generated by photolysis of such molecules as hexafluoroacetone (HFA), hexafluorazomethane (HFAM), trifluoromethyl iodide (TFMI) or trifluoroacetaldehyde (TFAA). With the exception of the photolysis of acetone itself, few other photodecompositions have been studied so extensively as that of hexafluoroacetone. (7,8) It is possible that both modes of decomposition shown below occur, although no thermochemical evidence is available to substantiate or disprove this.

$$\text{CF}_3\text{OCCF}_3 + \text{hv} \rightarrow \text{CF}_3\text{O} \cdot + \text{CF}_3' \cdot$$

$$\text{CF}_3\text{OCCF}_3 + \text{hv} \rightarrow 2\text{CF}_3' \cdot + \text{CO}$$

In view of the carbon-fluorine bond strength, however, (4) the decomposition:

$$\text{CF}_3\text{OCCF}_3 + \text{hv} \rightarrow \text{CF}_3\text{OCCF}_2' + \text{F}''$$
may safely be discounted.

HFA and HFAM have the advantage that the amount of carbon-monoxide or nitrogen formed provides a measure of the overall quantum yield. In both cases, however, CF₃ radicals may be lost by addition to the parent molecule. This is a serious disadvantage when a material balance method is to be employed.

\[
\text{CF}_3 \text{N} = \text{NCF}_3 + \text{CF}_3 \cdot \xrightarrow{\text{CF}_3} \text{N} - \text{N} - \text{CF}_3
\]

\[
\text{CF}_3 \text{C} = 0 + \text{CF}_3 \cdot \xrightarrow{\text{CF}_3} \text{CF}_3 \text{C} \text{CF}_3 \cdot \xrightarrow{\text{CF}_3} \text{CF}_3 \text{C} \text{O} - \text{CF}_3 \]

The reversibility of addition to the carbonyl group was demonstrated by Alcock and Whittle (11) who observed trifluoroacetone amongst the products from photolysis of HFA/CH₃I mixtures.

The photolysis of acetone or azomethane is widely used for the generation of methyl radicals. In both cases abstraction of hydrogen from the parent molecule is an important mode of reaction for the radicals formed.

\[
\text{CH}_3 \text{COCH}_3 + \text{CH}_3 \cdot \xrightarrow{\text{CH}_4 + \text{CH}_3 \text{COCH}_2 \cdot}
\]

\[
\text{CH}_3 \text{N}_2 \text{CH}_3 + \text{CH}_3 \cdot \xrightarrow{\text{CH}_4 + \text{CH}_3 \text{N}_2 \text{CH}_2 \cdot}
\]

Where the rate of formation of methane is used as an index of the rate of a reaction under study in the system, a correction must be made to allow for this. In some cases this may account for most of the methane formed, leading to
the possibility of serious accumulation of error in the desired rate constant. This difficulty is encountered with all sources of alkyl radicals. $\text{CF}_3^-$ radicals, however, will not abstract fluorine from trifluoromethyl groups (7,8,10), leading to much simpler systems. The photolysis of perfluorodiethyl ketone has been used as a source of $\text{C}_2\text{F}_5^-$ radicals (13) and again no abstraction of fluorine from the parent compound is observed. Similarly perfluorodi-n-propyl ketone represents a clean source of $\text{C}_3\text{F}_7^-$ radicals. (18)

$$\text{C}_3\text{F}_7\text{COC}_3\text{F}_7 + \text{hv} \rightarrow 2\text{C}_3\text{F}_7^- + \text{CO}$$

This split (Norrish type I) is the only mode of decomposition observed. No Norrish type II split

$$\text{C}_3\text{F}_7\text{COC}_3\text{F}_7 + \text{hv} \rightarrow \text{CF}_3\text{COC}_3\text{F}_7 + \text{C}_2\text{F}_4^-$$

has been reported.

Photolysis of trifluoroacetone yields CO, $\text{CH}_4$, $\text{C}_2\text{H}_6$, $\text{CF}_3\text{CH}_3$ and $\text{C}_2\text{F}_6$, with again no formation of $\text{CF}_4$ or $\text{CH}_3\text{F}$. Sieger and Calvert, who first studied this radical source, (19) proposed the following split as the major primary photolytic process:

$$\text{CF}_3\text{COCH}_3 + \text{hv} \rightarrow \text{CF}_3\text{CO}^- + \text{CH}_3^-$$

This is unlikely to be the case, however, since there is no evidence of the formation of products resulting from the trifluoroacetyl radical. In a more recent investigation (20) biacetyl was identified among the reaction products, suggesting that the principal mode of decomposition is:

$$\text{CH}_3\text{COCF}_3 + \text{hv} \rightarrow \text{CH}_3\text{CO}^- + \text{CF}_3^-$$
The yields of methane and ethane, however, indicate that
\[ \text{CH}_3\text{COOF}_3 + h\nu \rightarrow \text{CH}_3^\cdot + \text{CF}_3^\cdot + \text{CO} \]
may also occur to a significant extent.

Photolysis of TFMI (14) forms a convenient source of trifluoromethyl radicals, free from addition reactions with the parent molecule. The presence of iodine atoms in the system conveniently inhibits secondary reactions. This is discussed more fully in Chapter 3. Perfluoroethyl-iodide has also been used as a photolytic radical source (14).

Photolysis of perfluoroaldehydes would appear to provide a further useful source of fluorinated alkyl radicals, and is a widely used method of obtaining \(\text{C}_2\text{F}_5^\cdot\) and \(\text{C}_3\text{F}_7^\cdot\) (15,16,17). The principal reactions are normally taken to be:

1) \(\text{R}_f\text{CHO} + h\nu \rightarrow \text{R}_f^\cdot + \text{CHO}^\cdot\)
2) \(\text{R}_f^\cdot + \text{R}_f\text{CHO} \rightarrow \text{R}_f\text{H} + \text{R}_f\text{CO}^\cdot\)
3) \(\text{R}_f^\cdot + \text{R}_f^\cdot \rightarrow \text{R}_f^2\)

Dodd and Smith (17) photolysed trifluoroacetaldehyde and obtained an activation energy of 8.4 k.cal/mole for reaction 2. Later investigation of the photolysis of \(\text{C}_2\text{F}_5\text{CHO}\) and \(\text{C}_3\text{F}_7\text{CHO}\) by G.O. Pritchard and his co-workers (15) gave values of 4.5 and 4.0 k.cal/mole respectively for the activation energy, and they concluded that Dodd and Smith's result was "improbably high". One of the aims of the present work was to attempt to resolve this discrepancy, and it now appears that the reaction:
\[ RfCHO + h\nu \rightarrow RfH + CO \]

represents an important mode of decomposition. This is discussed fully in Chapter 7.

Alkyl radicals may similarly be produced by the photolysis of ketones, iodides, aldehydes and azo-compounds. There also exist a number of sources which are not yet available for generation of fluorinated radicals. These include the thermal decomposition of metal alkyls (dimethyl mercury, tetramethyl lead, etc.), (21,22,23), pyrolysis of alkyl nitrites, (24)

\[ RCH_2ONO \rightarrow RCH_2O^+ + NO \]

\[ R^* + HCHO \]

and the mercury photosensitised decomposition of alkanes (25).

e.g. \[ C_2H_6 + Hg6^3P_1 \rightarrow C_2H_6^* + Hg6^1S_0 \]

\[ C_2H_5^* + H^* \]

Di-tertiary-butyl peroxide is a useful source of methyl radicals (26) due to the instability of the t-butoxyl radical formed initially on thermal decomposition.

\[ (CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^* \]

\[ (CH_3)_3CO^* \rightarrow CH_3^* + CH_3COCH_3 \]

Diacetyl peroxide decomposes to give two acyloxy radicals which then further decompose to carbon dioxide and methyl radicals.
Chapter 3 includes a description of an unsuccessful attempt to extend the use of acyloxy radicals as alkyl radical precursors by the use of dimethylazodiformate as a radical source. It was thought that the following thermal decomposition might occur, with the formation of nitrogen and carbon dioxide providing a measure of the rate of formation of methyl radicals.

\[
\begin{align*}
\text{CH}_3\text{C}^{-}\text{O}^{-}\text{N}^{-} &= \text{N}^{-}\text{O}^{-}\text{C}-\text{CH}_3 \\
&\rightarrow 2\text{CH}_3\text{C}^{-}\text{O}^{-} + \text{N}_2
\end{align*}
\]

\[
\begin{align*}
2\text{CH}_3\text{C}^{-}\text{O}^{-} &\rightarrow 2\text{CH}_3^{-} + 2\text{CO}_2
\end{align*}
\]

Unfortunately this simple reaction scheme is not obeyed.

**COMBINATION OF FREE RADICALS**

The absolute rate constant for combination, \( k_c \), has been measured for a number of radicals. The method most commonly used is the rotating sector technique which has been fully described by Melville and Burnett (31). Essentially, the mean lifetime of radicals generated photolytically is determined using intermittent illumination, and hence, knowing the rate of release of radicals into the system, their concentration, and hence \( k_c \), may
be determined. Using this method absolute rate constants for recombination of $\text{CH}_3^*$ and $\text{CF}_3^*$ radicals have been measured.

METHYL: $\log_{10} k_c = 13.34$ \hspace{1cm} \text{(28,32,33)}

TRIPLUROMETHYL: $\log_{10} k_c = 13.36$ \hspace{1cm} \text{(35)}

($k_c$ is in mole$^{-1}$ cm.$^3$ sec.$^{-1}$)

Although there is some evidence (36) to suggest that these reactions may have a slight temperature dependence, no reliable values exist for the activation energies. It is well established, however, that these are extremely small, if not zero, (11,35,37,38) and, in accordance with current kinetic practice, the above rate constants are therefore assumed to be independent of temperature.

It is well established, however, that $k_c$ is pressure dependent. Combination of two radicals produces a "hot" molecule which, of course, possesses sufficient energy for decomposition.

\[ \text{R}^* + \text{R}^* \xrightarrow{M} \text{R}_2^* \xrightarrow{} \text{R}_2 \]

The lifetime of such a species is dependent on the number of vibrational degrees of freedom into which this energy may be dissipated. Thus the probability of stabilisation by collision rather than redissociation increases with the complexity of the radicals involved, (28,29,30). For methyl and trifluoromethyl radicals decomposition becomes negligible at pressures greater than about 10 torr.

The recombination of methyl radicals has been studied
by a number of other methods including direct sampling from a flow system into the chamber of a mass-spectrometer (39,40) measurement, using a sensitive diaphragm manometer of pressure changes resulting from the adiabatic temperature change which occurs during the photolysis of acetone (41,42) and pulsed photolysis, an intermittent illumination technique in which the period of illumination is shorter than in the rotating sector method by a factor of about 1000 (43). Results obtained substantiate the value of $k_c$ quoted above. These methods have not been applied to the combination of CF$_3^-$ radicals, however, and no absolute rate constants have been reported for the combination of higher perfluoroalkyl radicals.

As well as auto-combination reactions of this type, cross-combination can occur between two different radicals:

$$A^- + A^- \longrightarrow A_2 \quad (k_{aa})$$
$$A^- + B^- \longrightarrow AB \quad (k_{ab})$$
$$B^- + B^- \longrightarrow B_2 \quad (k_{bb})$$

According to the simple collision theory of chemical kinetics, the cross-combination ratio

$$\Phi = \frac{k_{ab}}{k_{aa}^\frac{1}{2} \cdot k_{bb}^{\frac{1}{2}}}$$

should equal 2 for reactions of zero activation energy. If we denote the rate of formation of $A_2$ by $R_{a2}$, etc., then it follows that:
For small alkyl and perfluoroalkyl radicals, cross-combination ratios close to 2 are in fact found, often over a considerable temperature range. (52,93)

From a study of the photolysis of mixtures of acetone and hexafluoroacetone Pritchard and Dacey reported a high, temperature-dependent value for the cross-combination ratio of methyl and trifluoromethyl radicals, which they explained by assigning an activation energy of about 2 kcal./mole to the recombination of $\text{CF}_3^\cdot$. A later study of this system by Giles and Whittle (38) revealed the formation of appreciable quantities of $\text{CH}_2 = \text{CF}_2$. This is explained by the following reaction scheme.

$$\begin{align*}
\text{CH}_3^\cdot + \text{CH}_3^\cdot & \rightleftharpoons \text{CH}_3\text{CF}_3^* \xrightarrow{k_e} \text{CH}_2 = \text{CF}_2 + \text{HF} \\
& \text{M} \xrightarrow{k_s} \text{CH}_3\text{CF}_3
\end{align*}$$

Thus the "hot" trifluoroethane molecule formed initially may be deactivated by collision, or may react by elimination of HF. If the cross-combination ratio is calculated using the combined rate of formation of $\text{CH}_3\text{CF}_3$ and $\text{CH}_2 = \text{CF}_2$ then, within experimental error, a value of 2 is obtained, which is independent of temperature. Elimination of hydrogen fluoride from activated fluoroethanes was first observed during the photolysis of 1,3-difluoroacetone (44). Similar reactions have been observed for the initial products of
combination of the following pairs of radicals.

\[
\begin{align*}
\text{CH}_3^\cdot + \text{CH}_2^2 \text{F}^\cdot ; & \quad \text{CH}_2^2 \text{F}^\cdot + \text{CF}_2 \text{H}^\cdot ; & \quad \text{CF}_2 \text{H}^\cdot + \text{CF}_2 \text{H}^\cdot ; \\
\text{CH}_3^\cdot + \text{CF}_2 \text{H}^\cdot ; & \quad \text{CH}_3^\cdot + \text{CH}_3 \text{CF}_2^\cdot ; & \quad \text{CH}_3^\cdot + \text{CF}_2 \text{HCH}_2^\cdot (45,46,47)
\end{align*}
\]

The Rice-Ramsperger-Kassel theory of unimolecular reactions has been used to calculate values of \(k_s/k_e\) for the various energised ethanes formed by combination of these radicals (46,48), leading to the conclusion that the probability of HF elimination decreases as the number of fluorine atoms in the molecule increases, the value of \(k_s/k_e\) for \(\text{C}_2\text{HF}_5\) being about 2000 times greater than that for \(\text{C}_2\text{H}_5\text{F}\). Quantitative predictions from this theory are in good agreement with experimental results. In particular Giles, Quick and Whittle, (49) who investigated the combination of \(\text{CF}_3^\cdot\) and \(\text{CF}_2 \text{H}^\cdot\), detected no perfluoroethylene among the products, showing that, as predicted, elimination is not, in fact, an important mode of reaction of the activated \(\text{C}_2\text{HF}_5\) molecule. No elimination of HF is reported for the following radical pairs. (16,50,51)

\[
\begin{align*}
\text{CH}_3^\cdot + \text{C}_3^2 \text{F}_7^\cdot ; & \quad \text{C}_2\text{H}_5^\cdot + \text{C}_3^2 \text{F}_7^\cdot ; & \quad \text{and} \quad \text{C}_2\text{H}_5^\cdot + \text{C}_2\text{F}_5^\cdot
\end{align*}
\]

It has been suggested (51) that the molecules formed on combination may possess enough vibrational degrees of freedom to dissipate the excess energy internally.

Ratios obtained for the cross-combination of alkyl radicals with perfluoroalkyls are commonly high, or temperature dependent (16,50,51,53). This has been attributed to polar effects (16), but in view of Whittle's
value for the cross-combination ratio of CF\textsubscript{3} and CH\textsubscript{3}; this explanation seems unsatisfactory. Results obtained in the course of the present work suggest that, for reactions involving ethyl or higher alkyl radicals, these anomalous values may be explained in terms of an alternative route to the cross-combination product, while re-examination of the published data for combination of CH\textsubscript{3} and C\textsubscript{3}F\textsubscript{7} casts grave doubts on the validity of the conclusions reached. This is discussed more fully in Chapter 8.

DISPROPORTIONATION REACTIONS

Although the strength of the carbon-fluorine bond precludes the occurrence of reactions such as:

\[ C_2F_5^- + C_2F_5^- \rightarrow CF_2 = CF_2 + C_2F_6 \]

cross-disproportionation reactions between alkyl and perfluoroalkyl radicals occur readily.

\[ e.g. \ C_2H_5^- + C_2F_5^- \rightarrow CH_2 = CH_2 + C_2F_5H \]

As mentioned above, however, an alternative route to the cross-combination product is thought to exist, which would invalidate published disproportionation/combination ratios for such reactions.

Partially fluorinated methyl radicals may undergo a type of disproportionation reaction in which a bi-radical is formed.

\[ e.g. \ CF_2H^- + CF_2H^- \rightarrow CF_2: + CF_2H_2 \quad (45, 55, 56) \]

while HF elimination, discussed above, may be regarded as
a disproportionation reaction.

e.g. $\text{CFH}_2 + \text{CFH}_2 \rightarrow \text{CFH} = \text{CH}_2 + \text{HF}$ (144)

**ADDITION REACTIONS**

The initial product from addition of a free radical to an unsaturated molecule is itself a radical.

$$\text{R} \cdot + \text{A} = \text{B} \rightarrow \text{RAB} \cdot$$

This may then react by abstraction, either from the radical source or from $\text{A} = \text{B}$, by a further addition step (which could give rise to a head-to-head or head-to-tail linkage), or by disproportionation or combination with another radical, $\text{R} \cdot$ or $\text{R(AB)}_n \cdot$. This leads to a large number of products of widely differing molecular weights, making complete product analysis impracticable.

In order to circumvent this difficulty Szwarc and his co-workers adopted a material balance method. HFAM was photolysed in the presence of 2,3-dimethylbutane, and the ratio $(\text{CF}_3\text{H}/\text{N}_2)_\text{BLANK}$ measured. The presence of an olefin $\text{A} = \text{B}$ in the system reduces this ratio due to the competing addition reaction.

$$\text{CF}_2\text{N}_2\text{CF}_3 \rightarrow 2\text{CF}_3 \cdot + \text{N}_2$$

$$\text{CF}_3 \cdot + \text{RH} \rightarrow \text{CF}_3\text{H} + \text{R} \cdot (k_a)$$

$$\begin{align*}
\text{CF}_3 \cdot + \text{A} = \text{B} \rightarrow \text{CF}_3\text{AB} \cdot (k_b)
\end{align*}$$

Taking these as the only reactions involving $\text{CF}_3 \cdot$ radicals;

$$\frac{k_b}{k_a} = \frac{[\text{RH}]}{[\text{A} = \text{B}]} \left\{ \frac{(\text{CF}_3\text{H}/\text{N}_2)_\text{BLANK}}{(\text{CF}_3\text{H}/\text{N}_2)_\text{OLEFIN}} - 1 \right\}$$
It is evident, however, that other reactions are possible, including abstraction from the olefin (allylic hydrogens being particularly labile), and radical-radical reactions such as

\[ \text{CF}_3\text{AB}^\cdot + \text{CF}_3^\cdot \rightarrow \text{CF}_3\text{ABCF}_3^\cdot \]

Using this method Szwarc studied the addition of trifluoromethyl radicals to a large number of unsaturated substances, obtaining values for \( E_a - E_b \) and \( A_b/A_a \). (57,58,59) When this work was carried out the only reported value for \( E_a \) was 1.7 k.cal/mole (60) leading to negative values of \( E_b \) for most of the systems studied. A recent re-investigation of the abstraction of hydrogen from 2,3-dimethylbutane by trifluoromethyl radicals has yielded a value of 3.3 k.cal/mole for \( E_a \) which is entirely compatible with the accepted value for abstraction by methyl radicals. Use of this more reliable activation energy leads to positive values of \( E_b \) in most cases, but not all. It therefore appears that \( \text{CF}_3^\cdot \) reactions neglected in this treatment lead to appreciable errors in the ratio \( k_b/k_a \). This is borne out by a recent investigation (61) of the photolysis of TFMl/ethylene mixtures in the presence of a large excess of hydrogen sulphide. The hydrogen atoms in \( \text{H}_2\text{S} \) are extremely labile, making abstraction the preferred mode of reaction of the \( \text{CF}_3\text{AB}^\cdot \) radical. Thus the formation of products of high molecular weight is inhibited, making complete product analysis possible. This direct method gives the following Arrhenius parameters for the reaction
\[
\text{CF}_3^* + \text{CH}_2 = \text{CH}_2 \rightarrow \text{CF}_3\text{CH}_2\text{CH}_2^*.
\]

\[E = 2.4 \text{ k.cal/mole. } \log_{10} A = 11.4 \text{ (mole}^{-1}\text{cm.}^3\text{sec.}^{-1})\]

By comparison Swarc obtained:

\[E = 1.0 \text{ k.cal/mole. } \log_{10} A = 11.0\]

The corresponding parameters for addition of methyl radicals to ethylene are: (94)

\[E = 6.8 \text{ k.cal/mole. } \log_{10} A = 11.1\]

Thus at room temperature the rate of addition of CF\textsubscript{3}\^* radicals to ethylene is about four thousand times that for CH\textsubscript{3}\^*. This is likely to be due mainly to dipole/induced-dipole attraction between the readily polarised olefin molecule and the highly polar attacking radical.

Whittle and his co-workers have investigated the addition of trifluoromethyl radicals to benzene and a large number of its substituted alkyl and halogen derivatives (62,63,64), using a material balance method based on the following reactions.

\[
\text{CF}_3\text{COGF}_3 + h\nu \rightarrow 2\text{CF}_3^* + \text{CO}
\]

\[
\text{CF}_3^* + \text{C}_6\text{H}_6 \rightarrow \text{CF}_3\text{H} + \text{C}_6\text{H}_5^* \quad (k_a)
\]

\[
\text{CF}_3^* + \text{C}_6\text{H}_6 \rightarrow \text{CF}_3\text{C}_6\text{H}_6^* \quad (k_b)
\]

\[
\text{CF}_3^* + \text{CF}_3^* \rightarrow \text{C}_2\text{F}_6 \quad (k_c)
\]

Neglecting the reaction \(\text{CF}_3\text{C}_6\text{H}_6^* + \text{CF}_3^* \rightarrow \text{CF}_3\text{C}_6\text{H}_6\text{CF}_3\),

\[
k_b = k_c^{\frac{1}{2}} \frac{2R_{\text{CO}} - R_{\text{CF}_3\text{H}} - 2R_{\text{C}_2\text{F}_6}}{R_{\text{C}_2\text{F}_6} [\text{C}_6\text{H}_6]}
\]
Trifluoromethyl radicals will also add to carbonyl and azo groups, as outlined previously in the discussion of radical sources. No reliable kinetic data exist for addition reactions of higher perfluoroalkyl radicals.

**ABSTRACTION REACTIONS**

Halogen atom abstraction from carbon tetrachloride, chloroform, dichloromethane, methylchloride, methylbromide and methyliodide by CF$_3$ radicals has been studied by Alcock and Whittle. ([11,65] Arrhenius parameters have also been reported [64]) for abstraction of halogen atoms from halobenzenes and toluenes by trifluoromethyl radicals. It is thought, however, that this is preceded by an addition reaction, with abstraction taking place from the addition complex.

\[
\text{i.e. } \text{CF}_3^+ + \text{ArX} \rightarrow \text{CF}_3\text{ArX}
\]

\[
\text{CF}_3^+ + \text{CF}_3\text{ArX} \rightarrow \text{CF}_3\text{X} + \text{ArCF}_3
\]

In all cases abstraction of chlorine was found to be an extremely difficult process, while as previously mentioned, no abstraction of fluorine has been observed.

Most research on transfer reactions of trifluoromethyl radicals, however, has dealt with hydrogen atom abstraction. If the reactions;

\[
\text{CF}_3^+ + \text{RH} \rightarrow \text{CF}_3\text{H} + \text{R}^+ \quad (k_a)
\]

and \[
\text{CF}_3^+ + \text{CF}_3^+ \rightarrow \text{C}_2\text{F}_6 \quad (k_c)
\]

are, respectively, the only source of fluoroform and hexafluoroethane, then we may define:
\[ R = \frac{k_a}{k_c} = \frac{R_{CF_3H}}{R_{O_2H}^t[RH]} \]

As mentioned in the section on radical combination reactions:

\[ k_c = 10^{13.36} \text{ mole}^{-1}\text{cm}^3\text{sec}^{-1} \]

\[ \therefore \log_{10} k_a = 6.68 + \log_{10} R \]

Now, expressing \( k_a \) in terms of the simple Arrhenius equation \( k = A\exp(-E/RT) \)

\[ \log_{10} k_a = \log_{10} A - (E/2.303RT) \]

\[ \log_{10} R = (\log_{10} A - 6.68) - (E/4.576T) \]

Thus a plot of \( \log_{10} R \) against \( 1,000/T \), where \( T \) is the absolute temperature, has intercept \((\log_{10} A - 6.68)\) and gradient \( E/4.576 \) where \( E \) is the activation energy for abstraction in k.cal/mole.

When the present work commenced (1966), a considerable amount of kinetic data had been obtained for abstraction by \( CF_3^- \) from hydrocarbons, and Arrhenius parameters had also been reported for abstraction from acetone, acetaldehyde, trifluoroacetone and trifluoroacetaldehyde (68). Whittle had also investigated the abstraction of hydrogen from a number of partially halogenated methane derivatives (11,12,66). With the exception of Arthur and Bell's work on hydrogen sulphide, (69) and a study by Carlton et al. (70) of abstraction from methanol and its deuterated derivatives, all available kinetic data referred to reactions in which only carbon-hydrogen bonds were severed. For this
reason reactions of \( \text{CF}_3^* \) with molecules containing OH, SH, NH and SiH as well as CH linkages were investigated. By studying polar molecules it has also been possible to observe the effects of dipole interactions with the strongly polar fluoroalkyl radicals. Since hydrocarbon molecules are virtually non-polar, little was known of the way in which such interactions affect Arrhenius parameters for hydrogen abstraction.

Considerably less work has been done on transfer reactions of higher perfluoroalkyl radicals. The reactions

\[
\begin{align*}
\text{R}_f^+ + \text{H}_2 & \rightarrow \text{R}_f\text{H} + \text{H}^+ \quad \text{and} \\
\text{R}_f^+ + \text{D}_2 & \rightarrow \text{R}_f\text{D} + \text{D}^+
\end{align*}
\]

have been studied for \( \text{R}_f^+ = \text{CF}_3^*, \text{C}_2\text{F}_5^*, \) and \( \text{n-C}_3\text{F}_7^- \). The extent to which reactions of the type

\[
\text{R}_f^+ + \text{H}^+ \rightarrow \text{R}_f\text{H}
\]

contribute to the \( \text{R}_f\text{H} \) yield is not known, however, making these results subject to considerable uncertainty. Arrhenius parameters have also been reported for the reaction of \( \text{C}_2\text{F}_5^- \) with methane (13), and \( \text{n-C}_3\text{F}_7^- \) with methane, ethane, cyclohexane and acetone. (16,53,74,76) Reactions of the type:

\[
\text{R}_f^+ + \text{R}_f\text{CHO} \rightarrow \text{R}_f\text{H} + \text{R}_f\text{CO}^-
\]

have already been dealt with in the discussion of radical sources.

An important unifying conclusion which emerged from the extensive study of abstraction from hydrocarbons by
CF₃ radicals is that the activation energy for such reactions is approximately 2.5 k.cal/mole lower than that for the corresponding abstraction by methyl radicals (77). When this work was carried out it was believed that the carbon-hydrogen bond dissociation energy for fluoroform, D(CF₃-H), was approximately 103 k.cal/mole, only slightly greater than D(CH₃-H), and an explanation of this activation energy difference based on the high polarity of the CF₃ radical was proposed (60). Later work by Whittle and his colleagues, (78), however suggested that a more probable value for D(CF₃-H) is 105 k.cal/mole. A value of 2.5 k.cal/mole for D(CF₃-H) - D(CH₃-H) is now entirely feasible, and it is unnecessary to invoke explanations based on polarity. There is an indication from available evidence that there exists a trend in radical reactivity in the order

\[
\text{CF}_3^+ > \text{C}_2\text{F}_5^+ > \text{C}_3\text{F}_7^+ > \text{CH}_3^+
\]

and that this is paralleled by a decrease in the strength of the carbon-hydrogen bond formed. (13,78) In the absence of sufficient kinetic data, however, this must be regarded as somewhat speculative.

In order to study the relative rates of hydrogen atom abstraction from different sites in the same molecule, deuterium labelling is frequently employed. The activation energy for abstraction of an atom of deuterium, however, is not the same as that for hydrogen. This arises from the fact that in the ground vibrational state a chemical bond possesses a finite vibrational energy known as the zero-point energy. The greater
inertial mass of a deuterium atom leads to a lower zero-point energy than would be associated with a hydrogen atom in the same environment. From this it follows that the activation energy for abstraction of deuterium should be higher than that for the corresponding hydrogen abstraction by the zero-point energy difference, $\Delta E_0$. For a C-H bond $\Delta E_0$ is 1.2 k.cal/mole, while for an N-H bond it is 1.3 k.cal/mole (79).

This elementary treatment of the kinetic isotope effect predicts that the pre-exponential Arrhenius parameter should be unaffected.

i.e. $A_H/A_D = 1$

and hence

$$k_H/k_D = e^{-\frac{\Delta E_0}{RT}}$$

Within the limits of experimental error this has been verified for a number of hydrogen and deuterium atom abstractions by methyl and trifluoromethyl radicals. (80-84)

It is common practice to assume that secondary isotope effects are negligible, (e.g. to assume that the rate constants for hydrogen atom abstraction from the amino groups in $\text{CH}_3\text{NH}_2$ and $\text{CD}_3\text{NH}_2$ will be the same). Experimental evidence supports the validity of this assumption (85-89).

The way in which kinetic data for abstraction from labelled and unlabelled molecules may be combined is illustrated by the following reactions of methylamine and trideuteromethylamine.
1. $\text{CD}_3\text{NH}_2 + \text{CF}_3^- \rightarrow \text{CF}_3^\text{D} + \cdot\text{CD}_2\text{NH}_2$
2. $\text{CD}_3\text{NH}_2 + \text{CF}_3^- \rightarrow \text{CF}_3\text{H} + \text{CD}_3\text{NH}^-$
3. $\text{CH}_3\text{NH}_2 + \text{CF}_3^- \rightarrow \text{CF}_3\text{H} + \cdot\text{CH}_2\text{NH}_2$
4. $\text{CH}_3\text{NH}_2 + \text{CF}_3^- \rightarrow \text{CF}_3\text{H} + \text{CH}_3\text{NH}^-$
5. $\text{CH}_3\text{NH}_2 + \text{CF}_3^- \rightarrow \text{CF}_3\text{H} + (\text{C}_2\text{H}_4\text{N})$

Reaction 5 represents overall abstraction from the undeuterated substrate.

i.e. $k_5 = k_3 + k_4$

But, neglecting secondary isotope effects,

$k_2 = k_4$ therefore $k_3 = k_5 - k_2$

The preceding elementary treatment of primary isotope effects predicts that:

$A_2/A_1 = 1$ and $E_1 - E_3 = \Delta E_0 = 1.2 \text{ k.cal/mole}$

This simple view of the processes involved, however, is complicated by an effect known as quantum-mechanical tunnelling. Classically, before reaction is possible the system must possess sufficient energy (the activation energy) to reach the activated complex between reactants and products. From a quantum-mechanical standpoint, however, there is a finite probability of reaction for systems of lower energy. This probability is greatest when the De Broglie wavelength of the species involved is comparable with the effective width of the potential barrier. Thus tunnelling is far less likely for deuterium than it is for hydrogen atoms, while the abstraction of larger atoms or groups in this way has not been observed.
Since the relative importance of tunnelling is greatest at low temperatures, the observed activation energy for hydrogen abstraction is likely to be an underestimate of the actual height of the potential energy barrier, possibly by as much as 20%. (68) Since the corresponding lowering will be considerably less in the case of deuterium, the occurrence of the tunnel effect should lead to values of $E_D - E_H$ greater than $\Delta E_o$ and values of $A_H/A_D$ less than unity, as has been observed by a number of workers. (90,91,92)

At present there is no general method which may be used to allow for the effects of tunnelling, and in accordance with general practice Arrhenius parameters obtained in the present work are reported without correction. It is evident, however, that this must be borne in mind when using such parameters for the calculation of bond strengths, or other molecular properties.

For an elementary chemical process the Arrhenius parameters for the reverse reaction ($E_r$ and $A_r$) may be derived thermochemically from those for the forward reaction. Firstly it is evident that:

$$E_r - E_r = \Delta H$$

The equilibrium constant for the reaction, $K$, is related to the change in free energy by the equation:

$$-RT \ln K = \Delta G = \Delta H - T\Delta S$$
But \( K = \frac{k_f}{k_r} = \frac{A_f}{A_r} \exp \left( -\frac{(E_f-E_r)}{RT} \right) \)

\[\therefore \ln K = \ln \left( \frac{A_f}{A_r} \right) - \frac{\Delta H}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \]

\[\therefore \ln \left( \frac{A_f}{A_r} \right) = \frac{\Delta S}{R} \]

\[\therefore \log A_r = \log A_f - \Delta S/4.576 \]

Using these relationships it has been possible to obtain estimates of Arrhenius parameters for abstraction of hydrogen from fluoroform. Although subject to accumulation of errors from the kinetic and thermochemical values employed, this approach gives access to kinetic data which are frequently unobtainable by direct methods.
CHAPTER 2

1. APPARATUS

The apparatus employed is shown diagrammatically in Fig. 1, using the following symbols:-

- 'HONE' VALVE
- TEFLOWN STOPCOCK
- GROUND GLASS STOPCOCK (straight through)
- GROUND GLASS STOPCOCK (right angled)
- GROUND GLASS STOPCOCK (three-way 'T' tap)
- GROUND GLASS STOPCOCK (two-way 'switch' tap)
- NEEDLE VALVE
- GROUND GLASS CONE
- GROUND GLASS SOCKET

A. VACUUM SYSTEM

A pyrex high vacuum system was constructed, the principal components being:

a) THE PUMPING SYSTEM: an EDWARDS "Speedivac" mercury diffusion pump, flanked by two detachable cold traps, and backed by an EDWARDS two stage rotary oil pump.

b) THE STORAGE MANIFOLD: three storage bulbs (with cold-fingers attached) of volume 2 litres, 1 litre, and 500 ml., a vacustat, and two ground-glass cones. All taps on this manifold are ground-glass stopcocks, lubricated with A PIEZON-'L' high vacuum hydrocarbon tap grease (A.E.I. Ltd.),
as is the cone and socket pivot of the vacustat.

c) THE MIXING MANIFOLD: a mercury manometer with mirror scale, a mixing bulb of approximate volume 150 ml., and a small tube for trapping

d) THE CENTRAL MANIFOLD: a low volume manifold, connected by stainless-steel valves with teflon seats (HONE INSTRUMENTS Ltd.) to the mixing manifold, pumping system, cold-trap (A), and chromatography u-tube, and to the reaction cell by a WESTF teflon stopcock with VITON rubber o-ring seals (WEST-Glass CORPORATION). The glass-metal seals to the Hone valves were made with ARALDITE epoxy-resin adhesive.

e) GAS MEASUREMENT AND TRANSFER SYSTEM:
A ground-glass stopcock lubricated with KEL-F-90 fluoro-carbon high vacuum tap grease (MINNESOTA MINING AND MANUFACTURING Co) joins the cold-trap (A) to a tube (B), which may be used as a sharing volume.

\[
\frac{\text{VOLUME OF (A)}}{\text{VOLUME OF (B)}} = 1.10 \pm 0.01
\]

Trap (A) is also connected by a Hone valve to the inlet arm of a Töpler pump. From the bulb of the Töpler pump gases may be driven, through a series of three-way taps, to:

i) a gas burette

ii) a sample tube attached to a B-14 socket, or

iii) the chromatography u-tube

Using the Töpler pump quantitative transfer may also be effected between any two of these.
The available gas-burette volumes are:

\[ \begin{align*}
OA &= 0.0722 \text{ cc} \\
OB &= 0.6214 \text{ cc} \\
OC &= 2.16 \text{ cc}
\end{align*} \]

where 0 is the top of the closed limb and A, B, and C are etched marks.

**B. GAS CHROMATOGRAPHY SYSTEM**

From the cylinder pressure-reduction head the carrier gas (B.O.C. hydrogen or helium) passes through the following:

a) a needle valve (EDWARDS)

b) the reference arm of a thermistor thermal conductivity detector (Th.C.D.) GOW-MAC MODEL 9677

c) EITHER the u-tube of the injection system OR a by-pass of glass capillary when the Hone valves to the u-tube are closed

d) EITHER column 1
   OR column 2

e) EITHER a flame ionisation detector (F.I.D.)
   OR the other arm of the thermal conductivity detector, in which case it then passes through

f) a bubble meter.

All ground-glass stopcocks in this system are spring-loaded to withstand pressures above atmospheric without unseating.

In most runs the measured products were eluted a considerable time before the unchanged reactants, or
products of higher molecular weight. To avoid long waiting periods between runs, the direction of flow through the columns was reversed after the required peaks had appeared. All columns used consisted of packed loops of 5 mm. O.D. pyrex tubing. The following packings were used:

- **SILICA GEL**: the 40-60 mesh fraction of B.D.H. silica gel activated by heating under vacuum.
- **ACTIVATED ALUMINA (100-120 mesh)** - Phase Separations Ltd.
- **DIETHYL ADIPATE ON FIREBRICK**: 40-60 mesh firebrick coated with 20% diethyladipate

The various combinations of column and operating conditions used are summarised in Table 1.

A potential of 270 V was maintained between the collector plate and jet of the flame ionisation detector, by three dry batteries wired in series. The ion current was amplified by a VIBRON ELECTROMETER, model 33B-2 (E.I.L.), used in conjunction with an E.I.L. shunt unit, type A49A, which provided seven tenfold attenuations.

The circuit used in conjunction with the thermal conductivity detector is shown in Fig. 2. The values shown for the attenuator resistances are nominal values only: the attenuator was calibrated empirically. In Table 4 are listed the reciprocal sensitivities, used as multiplicative factors for conversion of peak area on a given range to the corresponding peak area on the most sensitive range (RANGE 1).
<table>
<thead>
<tr>
<th>Packing</th>
<th>Packed</th>
<th>Length (m)</th>
<th>Temp (°C)</th>
<th>Carrier</th>
<th>Flow (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Silica Gel (40-60)</td>
<td></td>
<td>3</td>
<td>50</td>
<td>Hydrogen</td>
<td>25</td>
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<tr>
<td>B Silica Gel (40-60)</td>
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<td>4.5</td>
<td>50</td>
<td>Hydrogen</td>
<td>75</td>
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<tr>
<td>C Porapak-T</td>
<td></td>
<td>1.5</td>
<td>40</td>
<td>Hydrogen</td>
<td>35</td>
</tr>
<tr>
<td>D Porapak-T</td>
<td></td>
<td>1.5</td>
<td>60</td>
<td>Helium</td>
<td>25</td>
</tr>
<tr>
<td>E Alumina (100-120)</td>
<td></td>
<td>4.5</td>
<td>60</td>
<td>Helium</td>
<td>25</td>
</tr>
<tr>
<td>F Porapak-T + Porapak-Q</td>
<td></td>
<td>1.5</td>
<td>50</td>
<td>Helium</td>
<td>25</td>
</tr>
<tr>
<td>G Porapak-Q</td>
<td></td>
<td>1.5</td>
<td>50</td>
<td>Hydrogen</td>
<td>25</td>
</tr>
<tr>
<td>H Alumina (100-120)</td>
<td></td>
<td>1.5</td>
<td>60</td>
<td>Hydrogen</td>
<td>50</td>
</tr>
<tr>
<td>I Diethyl Adipate on Firebrick</td>
<td></td>
<td>10</td>
<td>0</td>
<td>Hydrogen</td>
<td>25</td>
</tr>
<tr>
<td>J Porapak-T + Porapak-Q</td>
<td></td>
<td>3 + 3</td>
<td>50</td>
<td>Hydrogen</td>
<td>40</td>
</tr>
<tr>
<td>SUBSTANCE</td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
</tr>
<tr>
<td>----------------------------</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Silane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexafluoroethane</td>
<td>6</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>9</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>14</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ethane</td>
<td>6</td>
<td>22</td>
<td>9</td>
<td>16</td>
<td>16</td>
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<tr>
<td>Fluoroform</td>
<td>13</td>
<td>5</td>
<td>11</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>Perfluoropropane</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluoro-n-Butane</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentafluoroethane</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso-Butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-Trifluoropropane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>But-1-ene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans But-2-ene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis But-2-ene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-Trifluoropentane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIG. 2. THERMISTOR DETECTOR CIRCUIT

Matched Thermistors (in gas stream)

100 OHM HELIPOT 10 mA. 50 OHMS.
3000 OHMS
500 OHMS 500 OHMS
1500 820 390 220 100 4.7 22 12 6.8 6.8
ATTENUATOR (Resistances - OHMS)

FIG. 3. FURNACE CIRCUIT

PROBE

FURNACE

VARICAN

2.5 AMP. METER BIKINI
### TABLE 3

**TYPICAL CHROMATOGRAPHY CALIBRATION**

<table>
<thead>
<tr>
<th>Volume (cc)</th>
<th>Pressure (torr)</th>
<th>Temp. (°K)</th>
<th>Amount (micro moles)</th>
<th>Peak Area (sq. ins.)</th>
<th>Attenuator Range Factor</th>
<th>Area (sq. ins.)</th>
<th>Amount Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA = 0.0722</td>
<td>117</td>
<td>298</td>
<td>0.455</td>
<td>8.03</td>
<td>1</td>
<td>1.000</td>
<td>8.03</td>
</tr>
<tr>
<td>OA = 0.0722</td>
<td>182</td>
<td>299</td>
<td>0.706</td>
<td>5.81</td>
<td>2</td>
<td>1.906</td>
<td>11.1</td>
</tr>
<tr>
<td>OB = 0.624</td>
<td>68</td>
<td>297</td>
<td>2.29</td>
<td>8.52</td>
<td>3</td>
<td>3.764</td>
<td>32.1</td>
</tr>
<tr>
<td>OB = 0.624</td>
<td>157</td>
<td>298</td>
<td>5.27</td>
<td>2.27</td>
<td>6</td>
<td>32.96</td>
<td>74.8</td>
</tr>
<tr>
<td>OB = 0.624</td>
<td>233</td>
<td>298</td>
<td>7.82</td>
<td>7.03</td>
<td>5</td>
<td>16.14</td>
<td>114</td>
</tr>
<tr>
<td>OC = 2.16</td>
<td>165</td>
<td>299</td>
<td>19.1</td>
<td>4.55</td>
<td>7</td>
<td>64.28</td>
<td>293</td>
</tr>
<tr>
<td>OC = 2.16</td>
<td>253</td>
<td>298</td>
<td>29.4</td>
<td>7.08</td>
<td>7</td>
<td>64.28</td>
<td>455</td>
</tr>
</tbody>
</table>

| Mean          |                |            |                      |                      |                        |                 |             |

The pressure of gas transferred to the u-tube is obtained directly from the difference in gas-burette readings before and after transfer.
CALIBRATION OF THERMISTOR DETECTOR

FIG. 4

MICROMOLES OF FLUOROFORM.

PEAK AREA. (Scale 1) SQ. INS.
### TABLE 4

<table>
<thead>
<tr>
<th>Range</th>
<th>Factor</th>
<th>Range</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.000</td>
<td>6</td>
<td>32.96</td>
</tr>
<tr>
<td>2</td>
<td>1.906</td>
<td>7</td>
<td>64.28</td>
</tr>
<tr>
<td>3</td>
<td>3.764</td>
<td>8</td>
<td>122.6</td>
</tr>
<tr>
<td>4</td>
<td>7.381</td>
<td>9</td>
<td>238.2</td>
</tr>
<tr>
<td>5</td>
<td>16.14</td>
<td>10</td>
<td>447.8</td>
</tr>
</tbody>
</table>

**KENT 1 mv. recorders were used with both detectors.** Peak areas were measured using an ALLBRIT fixed-arm planimeter.

Absolute calibration of either detector for a particular substance was achieved by measuring a sample in the gas-burette and transferring it quantitatively to the u-tube by Töpler pump.

**TYPICAL CHROMATOGRAPHY CALIBRATION**

The results of the calibration of the thermistor detector for fluoroform are detailed in Table 3 and presented graphically in Fig. 4. Since over this range there is obviously a linear relationship between peak area and amount of fluoroform, a mean value of AMOUNT/AREA is used as a conversion factor from peak area to yield.

Thus:

\[
1 \text{ SQ. IN. (SCALE 1)} = (0.066 \pm 0.002) \times 10^{-6} \text{ moles FLUOROFORM for a flow rate of 25 ml/min of HYDROGEN carrier and a thermistor detector current of 3 mA.}
\]
Although absolute calibrations were used in practice relative responses for a number of substances are listed in Table 2. The column headed Th.C.D. refers to the thermistor detector with HYDROGEN as carrier, while that headed F.I.D. refers to the flame-ionisation detector with air flowing at 750 ml/min (the standard flow-rate used throughout). Also shown in Table 2 are the absolute retention times of a number of substances under the various conditions listed in Table 1.

C. PHOTOLYSIS SYSTEM

(i) CELL

The reaction vessel was a quartz cylinder, (THERMAL SYNDICATE), of length 150 mm., and internal diameter 43 mm., with optically flat ends, and a side arm connected by graded seal to the pyrex vacuum system. The volume of the cylinder is 218 cc., while the side-arm and teflon stop-cock bring the total volume of the reaction vessel up to 222 cc.

(ii) FURNACE

The cell was housed in a heavy aluminium block furnace fitted with quartz end-plates. The temperature was controlled to within $\pm 0.2^\circ$ using the circuit shown in Fig. 3. and measured using a mercury thermometer calibrated against the boiling points of a number of pure substances over the temperature range employed for runs.
(iii) OPTICS

The full arc from a 220W HANOVIA mercury lamp (housed in a metal box fitted with a shutter) was collimated by a quartz lens to produce a parallel beam of light which fully illuminated the cell.

2. PROCEDURE

Reaction mixtures were made up on a pressure basis, each reactant in turn being trapped into the mixing bulb at -196°C. Mixing was effected by immersing the bulb in hot water, a measured pressure of the reaction mixture was expanded into the cell, and the residue trapped back into the bulb. Photolysis times were controlled using the shutter on the lamp box, and measured by stop-watch. Where analysis for all products to be measured could be carried out on a single column, the contents of the cell after reaction were trapped directly into the u-tube of the chromatography injection system; otherwise they were transferred initially to trap (A). By partition between (A) and (B) product analysis could be performed on two different columns. Alternatively the contents of (A) could be separated by low-temperature distillation, fractions being transferred by Töpler pump to the u-tube for analysis by gas chromatography, to a sample tube for analysis by mass-spectrometer, or to the gas-burette for measurement prior to analysis by either method.
The low temperature sources used in this work are shown in Table 5.

TABLE 5
LOW TEMPERATURE SOURCES

<table>
<thead>
<tr>
<th>Source</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ice/water</td>
<td>0</td>
</tr>
<tr>
<td>carbon tetrachloride slush</td>
<td>-23</td>
</tr>
<tr>
<td>chloroform slush</td>
<td>-63</td>
</tr>
<tr>
<td>acetone/cardice</td>
<td>-78</td>
</tr>
<tr>
<td>toluene slush</td>
<td>-95</td>
</tr>
<tr>
<td>n-propanol slush</td>
<td>-127*</td>
</tr>
<tr>
<td>iso-pentane slush</td>
<td>-160</td>
</tr>
<tr>
<td>liquid nitrogen</td>
<td>-196</td>
</tr>
</tbody>
</table>

* For most applications it was more satisfactory to use n-propanol slightly adulterated with iso-pentane, giving a temperature of about -130°C.

For thermal reactions runs were started by admitting the reactants to the cell, and stopped by trapping from the cell into (A) at -196°C. In systems involving deuterium labelling, the CF₂H and CF₂D formed were eluted together from the chromatography system, trapped out from the carrier gas by passage through a double loop of glass capillary at -196°C, and analysed by mass-spectrometer.
DARK REACTIONS

a) IN MIXING BULB

On mixing hexafluoroacetone with several of the hydrogen substrates studied, a marked reduction in total pressure was observed, and in some cases solid adducts were formed. For much of the work, therefore, trifluoromethyl iodide was used. This has the additional advantage of inhibiting secondary reactions. (See Chapter 3)

Before work was begun on a new substrate it was confirmed that no reduction in pressure occurred on mixing with the chosen radical source.

b) IN REACTION CELL

For each system involving a photolytic radical source at least one run was performed in which the normal run procedure was followed exactly, but the lamp was not unshuttered. In none of the systems studied was any dark reaction observed which led to the product measured.
3. CALCULATION OF RESULTS

A. INTERPRETATION OF MASS SPECTRA

Mass spectrometric analyses of gas mixtures were performed using an A.E.I. Ltd. MS-10 mass spectrometer. The data in Table 6 are taken from the manufacturers manual.

<table>
<thead>
<tr>
<th>Gas</th>
<th>CH₄</th>
<th>CO</th>
<th>O₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>7.69</td>
<td>12</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>14</td>
<td>15.6</td>
<td>14</td>
<td>32</td>
<td>28</td>
</tr>
<tr>
<td>15</td>
<td>85.8</td>
<td>16</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>100</td>
<td>28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S: 3.9  3.8  2.6  3.6

(where S is the sensitivity w.r.t. principal peak)

Before analysis of any sample a background spectrum was run, each peak being subtracted from the corresponding peak in the sample spectrum.
1) ANALYSIS OF PERMANENT GASES

a) In runs where di-tertiary-butyl peroxide or acetone was used as methyl radical source, the fraction volatile at -196°C was analysed for methane, carbon monoxide and any traces of air. Assuming a nitrogen/oxygen ratio of 3.6 for air, it follows that the contribution to the 28 peak from carbon monoxide,

\[
(CO^+) = 28 \text{ peak} - 5.0 \times (32 \text{ peak})
\]

\[
(CH_4^+) = 16 \text{ peak} - 0.17 \times (32 \text{ peak}) - 0.01 \times (CO^+)
\]

\[
\frac{(\text{METHANE})}{(\text{CARBON MONOXIDE})} = \frac{(CH_4^+)}{(CO^+)} \times \frac{3.8}{3.9}
\]

b) When azomethane was used as methyl radical source, analysis was made for methane, nitrogen and any traces of air.

In this case:

\[
(N_2^+) \text{ from nitrogen} = 28 \text{ peak} - 5.0 \times (32 \text{ peak})
\]

\[
(CH_4^+) = 16 \text{ peak} - 0.17 \times (32 \text{ peak})
\]

\[
\frac{(\text{METHANE})}{(\text{NITROGEN})} = \frac{(CH_4^+)}{(N_2^+) \text{ from nitrogen}} \times \frac{3.6}{3.9}
\]

2) ANALYSIS OF CF_3H/CF_3D MIXTURES

The 51 and 52 peaks may be accounted for as follows:

51 : CF_2H^+ 52 : 13CF_2H^+ and CF_2D^+

Since the normal ratio of isotopic abundances of 12C and 13C is 100 : 1.12, then assuming the same machine sensitivity for CF_3H and CF_3D,

\[
\frac{(CF_3H)}{(CF_3D)} = \frac{(51)}{(52)} - 0.0112 \times (51)
\]
B. TYPICAL RUNS

1. HYDROGEN ABSTRACTION BY TRIFLUOROMETHYL RADICALS

DATE: 30th April 1968

RUN NUMBER: 419

Pressure of H.F.A. in mixture = 112.6 torr \((P_1)\)
Pressure of H.F.B.A. in mixture = 56.8 torr \((P_2)\)
Total pressure = 169.4 torr
Pressure of mixture in cell = 68.0 torr \((P_3)\)

(Where H.F.A. is hexafluoroacetone and H.F.B.A. is heptafluorobutyraldehyde)

Furnace temperature, \(T = 126.8^\circ C = 400.0^\circ K\)
Photolysis time = 15 mins. = 900 secs.

\(\text{CF}_3H:\)

PEAK AREA = 3.19 sq. ins.
\(F = 2.268 \times 10^{-6} \text{ moles/sq.in.}\)

\(\text{C}_2\text{F}_6:\)

PEAK AREA = 2.36 sq. ins.
\(F = 3.523 \times 10^{-6} \text{ moles/sq.in.}\)

(Where \(F = \text{calibration factor}\))

Volume of cell = 222 cc.

Rate of formation of \(\text{CF}_3H = \frac{3.19 \times 2.268 \times 10^{-6}}{222 \times 900} \cdot \frac{36.2 \times 10^{-12} \text{ moles cm}^{-3} \text{sec}^{-1}}{}}

\(= 36.2 \times 10^{-12} \text{ moles cm}^{-3} \text{sec}^{-1}\)
Rate of formation of $C_2F_6 = \frac{2.36 \times 3.523 \times 10^{-6}}{222 \times 900}$

\[= 41.61 \times 10^{-12} \text{ moles cm}^{-3} \text{ sec}^{-1}\]

\[\sqrt{41.61 \times 10^{-2}} = 6.45 \times 10^{-6}\]

Pressure of H.F.B.A. in cell initially = $68.0 \times \frac{56.8}{169.4}$

Now, 760 torr, at $273.2^\circ K = 1$ mole per 22,400 cc.

\[\therefore \text{Initial conc. of H.F.B.A.} = \frac{1}{22400} \times \frac{56.8 \times 68.0}{196.4 \times 760} \times \frac{273.2}{400.0}\]

\[= \frac{56.8 \times 68.0}{169.4} \times \frac{16.05}{400.0} \times 10^{-6}\]

\[= 915 \times 10^{-6} \text{ moles cm}^{-3}\]

**ALDEHYDE USED = FLUOROFORM PRODUCED**

\[\therefore \text{Change in H.F.B.A. conc. during run}\]

\[= \frac{3.19 \times 2.268}{222} \times 10^{-6}\]

\[= 0.032 \times 10^{-6} \text{ moles cm}^{-3}\]

**Mean concentration**

\[= (915 - 0.16) \times 10^{-6}\]

\[= 899 \times 10^{-6} \text{ moles cm}^{-3}\]

Thus, using the relationship derived on page 26

\[R = \frac{36.2}{6.45 \times 899} = 6.25\]

\[\frac{1000}{T} = 2.500 \quad \log_{10}R = 0.796\]

(51)
2. HYDROGEN ABSTRACTION BY METHYL RADICALS

DATE: 28th January 1969

RUN NUMBER: 568

Pressure of azomethane in mixture = 8.7 torr
Pressure of tetramethyldisilane in mixture = 279.1 torr
Total pressure = 287.8 torr
Pressure of mixture in cell = 92.9 torr

Furnace temperature, \( T = 161.6^\circ C = 434.8^\circ K \)
Photolysis time = \( 2\frac{1}{4} \) mins = 135 secs.

\( \text{C}_2\text{H}_6: \)

Peak Area = 3.26 sq. ins.

\[ F = 0.0744 \times 10^{-6} \text{moles/sq. in.} \]

Amount of \( \text{C}_2\text{H}_6 \) formed = \( 3.26 \times 0.0744 \times 10^{-6} \)

\[ = 0.243 \times 10^{-6} \text{moles} \]

Initially:

(Azomethane) \[ = \frac{8.7}{287.8} \times \frac{92.9}{1} \times \frac{16.05}{434.8} \] (as above)

\[ = 0.104 \times 10^{-6} \text{moles cm}^{-3} \]

(Tetramethyldisilane) \[ = \frac{279.1}{287.8} \times \frac{92.9}{1} \times \frac{16.05}{434.8} \]

\[ = 3.325 \times 10^{-6} \text{ moles cm}^{-3} \]

PRODUCTS VOLATILE AT \(-196^\circ C\)

Volume: \( 0A = 0.0722 \text{ cm}^3 \)
Pressure = 161 torr
Temperature = \( 29^\circ C = 302^\circ K \)

Amount = \[ \frac{0.0722}{22400} \times \frac{273}{302} \times \frac{161}{760} = 0.617 \times 10^{-6} \text{ moles} \]
MASS SPECTRAL ANALYSIS

<table>
<thead>
<tr>
<th>m/e</th>
<th>Background</th>
<th>Sample</th>
<th>Corrected Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>1.4</td>
<td>563</td>
<td>562</td>
</tr>
<tr>
<td>28</td>
<td>21.7</td>
<td>1241</td>
<td>1219</td>
</tr>
<tr>
<td>32</td>
<td>0.0</td>
<td>3.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

It was shown on page 49 that \((N_2^+)^{-}\) from nitrogen

\[
\text{It} = (\text{corrected 28 peak}) - 5 \text{ (corrected 32 peak)}
\]

\[
= 1219 - 16 = 1203
\]

\((\text{CH}_3^+)\) = \((\text{corrected 16 peak}) - 0.17 \text{ (corrected 32 peak)}
\]

\[
= 562 - 0.6 = 561
\]

\[
\frac{\text{(Methane)}}{\text{(Nitrogen)}} = \frac{561}{1203} \times \frac{3.6}{3.9} = 0.430
\]

\[
\% \text{ Methane} = \frac{0.430}{1.430} = 30.1\
\]

Methane yield = \(0.617 \times 0.301 = 0.186 \times 10^{-6}\) moles

Nitrogen yield = \(0.617 \times 0.699 = 0.431 \times 10^{-6}\) moles

:\Ethane formed in primary photolysis process

\[
= 0.431 \times 0.007 = 0.003 \times 10^{-6}\) moles
\]

Ethane formed from combination of methyl radicals

\[
= 0.243 - 0.003 = 0.240 \times 10^{-6}\) moles
\]

\((\text{Volume of cell} = 222 \text{ cm}^3)\)

Rate of formation of ethane by combination

\[
= \frac{0.240 \times 10^{-6}}{222 \times 135} = 8.01 \times 10^{-12}\text{ moles cm}^{-3}\text{sec}^{-1}
\]

\[
\sqrt{8.01 \times 10^{-12}} = 2.83 \times 10^{-6}
\]
Total rate of formation of methane

\[
\text{Total rate of formation of methane} = \frac{0.186 \times 10^{-6}}{222 \times 135} = 6.21 \times 10^{-12} \text{ moles cm}^{-3} \text{ sec}^{-1}
\]

R for abstraction of hydrogen from azomethane by methyl radicals = 4.0 at 161°C (See page 76)

Rate of formation of methane by abstraction from azomethane = \( R \times (\text{azomethane}) \times \sqrt{\text{Rate of formation of ethane from radicals}} \)

\[
= 4.0 \times 10^{-14} \times 2.83
\]

\[
= 1.18 \times 10^{-12} \text{ moles cm}^{-3} \text{ sec}^{-1}
\]

Rate of formation of methane by abstraction from tetramethylsilane = 6.21 - 1.18

\[
= 5.03 \times 10^{-12} \text{ moles cm}^{-3} \text{ sec}^{-1}
\]

It is evident that the concentration of tetramethylsilane is effectively constant throughout the run, hence, using the relationship derived on page 26

\[
R = \frac{5.03}{2.83 \times 3.325} = 0.535
\]

\[
\frac{1000}{T} = 2.300 \quad \log_{10} R = 1.728
\]
4. MATERIALS

TRIFLUOROMETHYL IODIDE was obtained from two different sources.

a) Chromatographic analysis of the gas purchased from PIERCE CHEMICAL CO. revealed the presence of hexafluoroethane, fluoroform and carbon dioxide as impurities. These were removed by pumping at -130°C. The gas was then distilled at -63°C, and stored at -196°C in a blackened bulb on the vacuum line. It was further shown to be free from any hydrogen containing impurities by extensive photolysis of a sample of the iodide, when hexafluoroethane was formed in appreciable yield, but no measurable amount of fluoroform was produced.

b) Silver trifluoroacetate (KOCH-LIGHT) was intimately mixed with three times its own weight of iodine and heated, under slightly reduced pressure, with a free flame. The gases evolved were passed through a reflux condenser to remove most of the iodine vapour, and collected at -196°C. The fraction volatile between -63°C and -130°C was purified and stored as above.

\[
CF_3COOAg + I_2 \rightarrow CF_3I + AgI + CO_2
\]

HEXAFLUOROACETONE was obtained from two different sources.

a) Chromatographic analysis of the gas purchased from DU PONT CO. revealed the presence of hexafluoroethane, fluoroform, carbon dioxide, and a further impurity
tentatively identified as tetrafluoroethylene from its retention time. The gas was purified, stored, and the purity verified as in the case of the commercially obtained trifluoromethyl iodide.

b) Hexafluoroacetone sesquihydrate (KOCH-LIGHT) was dehydrated by dropping it onto a stirred mixture of phosphorus pentoxide and concentrated sulphuric acid at about 90°C. The gas evolved was trapped at -196°C, and the fraction volatile between -63°C and -130°C purified and stored as above.

TRIFLUOROACETALDEHYDE was prepared by dehydration of its hydrate (KOCH-LIGHT) using phosphorus pentoxide/sulphuric acid mixture as above. The purity of the fraction volatile between -63°C and -130°C was established by comparison of its I.R. spectrum with that in the literature, (34) and by the absence of impurities (especially hexafluoroethane and fluoroform) as shown by chromatographic analysis.

PENTAFLUOROPROPIONALDEHYDE and HEPTAFLUOROBUTYRALDEHYDE were prepared from their hydrates. (EASTMAN-KODAK) and purified in the same way.

AMMONIA: Distilled anhydrous ammonia (99.98%, I.C.I. Agricultural Division) was distilled between -95°C and -130°C and used without further purification.
DIMETHYLAMINE-d was prepared by shaking 10 ml. of deuterium oxide, acidified with a few drops of hydrochloric acid, with 1 atmosphere of dimethylamine (B.D.H.) in a closed 1 litre bulb for 24 hours. The partially deuterated amine was distilled from the bulb, and the process repeated with a further 10 ml. of acidified heavy water. The amine was then distilled from the bulb (at room temperature) into a trap at -196°C, and the fraction volatile between -63°C and -95°C was trapped into a storage bulb on the vacuum line.

A gas-phase I.R. cell with sodium chloride endplates was attached to the vacuum line by means of the B-14 cone, and pumped down. A measured pressure of undeuterated dimethylamine was admitted to the I.R. cell, and the transmittance at 730 cm\(^{-1}\) determined using an INFRACORD spectrometer. This procedure was repeated for a number of pressures, and a graph drawn of percent transmittance against pressure of dimethylamine in the cell. (Fig. 5) On deuteration the 730 cm\(^{-1}\) band shifts to 587 cm\(^{-1}\) (83), thus providing a means of determining the percentage exchange which has occurred.

The deuterated amine was then expanded into the storage, mixing and central manifolds, the I.R. cell, mixing bulb and reaction cell, and left to stand in the line for several days to allow exchange reactions between the amine and any hydrogen-containing substances adsorbed onto the walls of the vacuum system to reach equilibrium.
FIG. 5.

DEUTERATION OF DIMETHYLAMINE - CALIBRATION GRAPH

Variation of Transmittance at $730\text{cm}^{-1}$ with Pressure of Undeuterated Dimethylamine in I.R. Cell.

\[ \text{% Transmittance at } 730 \text{ cm}^{-1} \]

\[ \text{Dimethylamine Pressure (Torr.)} \]
It was then trapped back into the storage bulb, thoroughly degassed, and a measured pressure expanded into the I.R. cell. The transmittance at 730 cm\(^{-1}\) was measured as before, and a second determination performed using a different pressure of amine in the cell. From the calibration graph the pressure of undeuterated amine in each sample could be determined, and hence the extent of deuteration was derived as shown below.

<table>
<thead>
<tr>
<th>PRESSURE (mm.) IN CELL</th>
<th>% TRANSMITTANCE AT 730 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>56</td>
</tr>
<tr>
<td>CALIBRATION WITH DIMETHYLAMINE</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>45</td>
</tr>
<tr>
<td>10.6</td>
<td>35</td>
</tr>
<tr>
<td>15.7</td>
<td>24</td>
</tr>
<tr>
<td>DEUTERATED SAMPLE a)</td>
<td>17.1</td>
</tr>
<tr>
<td>b) 19.4</td>
<td>42</td>
</tr>
</tbody>
</table>

a) From calibration graph, pressure of dimethylamine (undeuterated) in cell = 6.35 mm. therefore, \(\%\) undeuterated = \(\frac{6.35}{17.1} \times 100 = 37.1\%\)

b) From graph, pressure of dimethylamine in cell = 7.1 mm. therefore, \(\%\) undeuterated = \(\frac{7.1}{19.4} \times 100 = 36.6\%\)

**THUS:** DIMETHYLAMINE = 37\% of sample, and

DIMETHYLAMINE-d = 63\%
METHYLAMINE was prepared from the hydrochloride salt (B.D.H.) by dropping a saturated solution of caustic potash onto a saturated aqueous solution of the salt heated to about 80°C and stirred with a magnetic stirrer. The product was collected at -196°C, and the fraction volatile between -78°C and -130°C was again distilled between -95°C and -196°C to ensure that no traces of water remained.

TRIDEUTEROMETHYLAMINE was prepared from the hydrochloride (E. MERCK, A.G. DARMSTADT) in the same way. The isotopic purity of better than 99% was confirmed by mass-spectral analysis.

AZOMETHANE was prepared by the oxidation of sym-dimethylhydrazine with mercuric oxide. (5,6). Dimethylhydrazine hydrochloride (ALDRICH CHEMICAL Co.) was dissolved in the minimum amount of water, and neutralised to litmus by the addition of solid caustic potash. This solution was added dropwise to a magnetically stirred slurry of mercuric oxide in water, and the gas evolved was collected at -196°C. After the addition was completed, the temperature was raised to about 80°C to drive over dissolved azomethane. The fraction volatile between -63°C and -130°C was stored at -196°C in a blackened bulb on the vacuum line. It was shown to be free from carbon dioxide and ethane by chromatographic analysis.
ETHANE purchased from B.O.C. was found to contain about 2% ethylene. This was removed by passing the gas through a column of bromine on charcoal. Traces of bromine were then removed by scrubbing with aqueous caustic soda, and the fraction volatile between -130°C and -196°C was collected. Chromatographic analysis revealed no impurities.

SILANE was prepared by dropping tetrachlorosilane (HOPKIN and WILLIAMS Ltd.) onto a stirred slurry of lithium aluminium hydride in diglyme at 0°C, under half an atmosphere of dry, oxygen-free nitrogen (B.O.C. 'spot' nitrogen passed through a column of molecular sieve). The product was passed through two traps at -78°C to remove solvent vapour, and collected at -196°C. The purity of the fraction volatile between -160°C and -196°C was verified by I.R., showing the absence of tetrachlorosilane, by mass spectroscopy, showing the absence of hydrogen chloride, carbon dioxide and nitrogen, and by gas chromatography which revealed no other impurities.

TRIMETHYLSILANE was similarly prepared by reduction of trimethylchlorosilane (HOPKIN and WILLIAMS Ltd.) at room temperature. The purity of the fraction volatile between -95°C and -130°C was verified by gas chromatography, I.R., and mass spectroscopy, as above.
The following commercial products were degassed and used without further purification.

n-BUTANE MATHESON (C.P. GRADE)
ETHYLENE " " "
BUT-1-ENE " " "
cis-BUT-2-ENE " " "
trans-BUT-2-ENE " " "
FLUOROFORM " " "
HEXAPFLUOROETHANE DU PONT
TRIDEUTEROMETHANOL MERCK, SHARP and DOHME
METHANOL B.D.H. (SPECTROSCOPIC GRADE)
CYCLOHEXANE " " "
ACETONE " " "
TETRAMETHYLSILANE " (N.M.R. GRADE)
DIMETHYLAMINE "
TRIMETHYLAMINE "
ETHYLENEIMINE KOCH-LIGHT
Di-tert-BUTYL PEROXIDE " "

BENZIL (KOCH-LIGHT) and DIMETHYLFORMAMIDE (EASTMAN-KODAK) were used without purification.
In certain systems products occurred which were not readily available commercially, and for which there was no simple preparation. In order to obtain samples for calibration of the detector, such substances were trapped out from the chromatography carrier gas. This was done by passing the gas emerging from the thermal conductivity detector through a double loop of glass capillary, which was immersed in liquid nitrogen at the onset of the peak in question. After trapping, the samples were distilled between $-63^\circ$C and $-130^\circ$C in order to free them from water and carbon dioxide present in the carrier gas.

The following substances were prepared in this way:-

PENTAFLUOROETHANE
PERFLUORO-n-BUTANE
PERFLUOROPROPANE
1,1,1-TRIFLUOROPROPANE
Hexafluoroacetone has been widely used as a photolytic source of $\text{CF}_3^-$ radicals. On mixing with methylamine, however, a white crystalline solid was immediately formed, while with trimethylamine a large drop in pressure occurred on mixing, an oily film being formed on the walls of the mixing vessel. Similar evidence of adduct formation was found when HFA was mixed with ammonia, dimethylamine, methanol and methyl mercaptan. Considerable reduction in pressure was also observed on mixing a small sample of hexafluoroazomethane with the above amines, and no further investigation of this radical source was undertaken.

$\text{CF}_3\text{I}$ showed no sign of adduct formation with hydrocarbons, amines, alcohols, aldehydes, mercaptans, silanes, ethyleneimine or ammonia.

In order to assess its suitability as a radical source it was photolysed alone, and in the presence of cyclohexane. In the former case the only gaseous product detected was hexafluoroethane, which is consistent with the following simple reaction scheme.

$$
\begin{align*}
\text{CF}_3\text{I} + h\nu & \rightarrow \text{CF}_3^- + \text{I}^- \\
\text{CF}_3^- + \text{CF}_3 & \rightarrow \text{C}_2\text{F}_6 \quad (k_o) \\
\text{I}^- + \text{I}^- & \rightleftharpoons \text{I}_2 \\
\text{CF}_3^- + \text{I}_2 & \rightarrow \text{CF}_3\text{I} + \text{I}^- \\
\text{CF}_3^- + \text{I}^- & \rightarrow \text{CF}_3\text{I}
\end{align*}
$$
### TABLE 7

Photolysis of TFMI in the Presence of CYCLOHEXANE

<table>
<thead>
<tr>
<th>RUN</th>
<th>T (°K)</th>
<th>t (sec)</th>
<th>C₆H₁₂</th>
<th>TFMI</th>
<th>CF₃H</th>
<th>C₂F₆</th>
<th>R</th>
<th>1000/T</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>357.0</td>
<td>300</td>
<td>0.272</td>
<td>1.75</td>
<td>14.4</td>
<td>1.88</td>
<td>38.5</td>
<td>2.80</td>
<td>1.586</td>
</tr>
<tr>
<td>55</td>
<td>357.1</td>
<td>300</td>
<td>0.211</td>
<td>1.65</td>
<td>11.6</td>
<td>2.07</td>
<td>38.5</td>
<td>2.80</td>
<td>1.585</td>
</tr>
<tr>
<td>54</td>
<td>357.2</td>
<td>300</td>
<td>0.250</td>
<td>1.92</td>
<td>14.7</td>
<td>2.30</td>
<td>38.9</td>
<td>2.80</td>
<td>1.589</td>
</tr>
<tr>
<td>53</td>
<td>370.3</td>
<td>600</td>
<td>0.257</td>
<td>1.98</td>
<td>14.7</td>
<td>1.25</td>
<td>51.1</td>
<td>2.70</td>
<td>1.708</td>
</tr>
<tr>
<td>52</td>
<td>370.3</td>
<td>600</td>
<td>0.265</td>
<td>1.96</td>
<td>15.1</td>
<td>1.20</td>
<td>52.0</td>
<td>2.70</td>
<td>1.716</td>
</tr>
<tr>
<td>47</td>
<td>370.3</td>
<td>1200</td>
<td>0.235</td>
<td>1.41</td>
<td>11.0</td>
<td>6.40</td>
<td>58.5</td>
<td>2.70</td>
<td>1.767</td>
</tr>
<tr>
<td>56</td>
<td>384.6</td>
<td>450</td>
<td>0.193</td>
<td>1.51</td>
<td>17.2</td>
<td>1.23</td>
<td>80.6</td>
<td>2.60</td>
<td>1.906</td>
</tr>
<tr>
<td>57</td>
<td>385.1</td>
<td>300</td>
<td>0.309</td>
<td>1.84</td>
<td>25.8</td>
<td>2.07</td>
<td>58.1</td>
<td>2.60</td>
<td>1.764</td>
</tr>
<tr>
<td>49</td>
<td>400.2</td>
<td>300</td>
<td>0.331</td>
<td>1.69</td>
<td>37.1</td>
<td>1.44</td>
<td>93.5</td>
<td>2.50</td>
<td>1.970</td>
</tr>
<tr>
<td>48</td>
<td>400.0</td>
<td>1200</td>
<td>0.214</td>
<td>1.29</td>
<td>16.7</td>
<td>4.53</td>
<td>115</td>
<td>2.50</td>
<td>2.062</td>
</tr>
<tr>
<td>59</td>
<td>416.7</td>
<td>180</td>
<td>0.158</td>
<td>1.80</td>
<td>33.7</td>
<td>2.33</td>
<td>139</td>
<td>2.40</td>
<td>2.144</td>
</tr>
<tr>
<td>58</td>
<td>416.7</td>
<td>300</td>
<td>0.285</td>
<td>1.70</td>
<td>39.5</td>
<td>1.49</td>
<td>113</td>
<td>2.40</td>
<td>2.054</td>
</tr>
<tr>
<td>75</td>
<td>434.8</td>
<td>100</td>
<td>0.238</td>
<td>1.53</td>
<td>75.3</td>
<td>2.51</td>
<td>200</td>
<td>2.30</td>
<td>2.300</td>
</tr>
<tr>
<td>60</td>
<td>434.8</td>
<td>100</td>
<td>0.156</td>
<td>1.77</td>
<td>55.6</td>
<td>3.06</td>
<td>204</td>
<td>2.30</td>
<td>2.309</td>
</tr>
<tr>
<td>51</td>
<td>435.2</td>
<td>160</td>
<td>0.240</td>
<td>1.77</td>
<td>63.6</td>
<td>1.67</td>
<td>205</td>
<td>2.30</td>
<td>2.312</td>
</tr>
<tr>
<td>50</td>
<td>434.7</td>
<td>300</td>
<td>0.303</td>
<td>1.55</td>
<td>56.4</td>
<td>1.01</td>
<td>185</td>
<td>2.30</td>
<td>2.266</td>
</tr>
</tbody>
</table>

### TABLE 8

Photolysis of HFA in the Presence of CYCLOHEXANE

<table>
<thead>
<tr>
<th>Run</th>
<th>T (°K)</th>
<th>t (sec)</th>
<th>C₆H₁₂</th>
<th>HFA</th>
<th>CF₃H</th>
<th>C₂F₆</th>
<th>R</th>
<th>1000/T</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>357.0</td>
<td>60</td>
<td>0.251</td>
<td>1.77</td>
<td>148</td>
<td>31.6</td>
<td>105</td>
<td>2.80</td>
<td>2.020</td>
</tr>
<tr>
<td>78</td>
<td>370.4</td>
<td>30</td>
<td>0.238</td>
<td>1.68</td>
<td>263</td>
<td>50.1</td>
<td>156</td>
<td>2.70</td>
<td>2.193</td>
</tr>
<tr>
<td>73</td>
<td>400.3</td>
<td>60</td>
<td>0.206</td>
<td>1.88</td>
<td>322</td>
<td>29.7</td>
<td>287</td>
<td>2.50</td>
<td>2.458</td>
</tr>
<tr>
<td>74</td>
<td>434.8</td>
<td>30</td>
<td>0.184</td>
<td>1.68</td>
<td>664</td>
<td>48.8</td>
<td>525</td>
<td>2.30</td>
<td>2.712</td>
</tr>
</tbody>
</table>

C₆H₁₂, TFMI and HFA are in 10⁻⁶ mole cm⁻³.

CF₃H and C₂F₆ are in 10⁻¹² mole cm⁻³ sec⁻¹.
On addition of cyclohexane, fluoroform was also formed, and may be attributed to the reaction:

\[ \text{CF}_3^+ + C_6H_{12} \rightarrow \text{CF}_3H + C_6H_{11}^- \]  \hspace{1cm} (k_a)

The rate constants obtained for this reaction were in reasonable agreement with those previously reported by Charles and Whittle (62) using HFA as radical source. For internal consistency, however, a few runs were performed using the ketone and, as shown in Fig. 6 the rate constants obtained were higher than those from the iodide runs by an amount appreciably in excess of experimental error. In order to investigate this discrepancy further, it was decided to carry out a more extensive product analysis, to elucidate the mode of reaction of the alkyl radical formed by abstraction. Chromatographic analysis was complicated by the relatively high molecular weight of cyclohexane, and so n-butane was used. Again, as may be seen from Fig. 6, consistently higher rate constants were obtained when HFA was used as radical source.

The product distribution from a typical ketone run is shown below:

<table>
<thead>
<tr>
<th>Product</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexafluoroethane</td>
<td>8.9%</td>
</tr>
<tr>
<td>Fluoroform</td>
<td>68.8%</td>
</tr>
<tr>
<td>But-1-ene</td>
<td>1.8%</td>
</tr>
<tr>
<td>trans-But-2-ene</td>
<td>1.2%</td>
</tr>
<tr>
<td>cis-But-2-ene</td>
<td>0.7%</td>
</tr>
<tr>
<td>C_4H_9CF_3 (total)</td>
<td>18.5%</td>
</tr>
</tbody>
</table>
FIG. 6.

**CF₃ ATTACK ON HYDROCARBONS**

- **USING HFA AS RADICAL SOURCE**
  - Upper Curve: - Cyclohexane
  - Lower Curve: - n-Butane.

- **USING TFMI AS RADICAL SOURCE**
  - Upper Curve: - Cyclohexane
  - Lower Curve: - n-Butane.
### TABLE 9

Photolysis of HFA in the Presence of n-BUTANE

<table>
<thead>
<tr>
<th>Run</th>
<th>(T(°K))</th>
<th>(t(\text{sec}))</th>
<th>(C_4H_{10})</th>
<th>HFA</th>
<th>(CF_3H)</th>
<th>(C_2F_6)</th>
<th>(R)</th>
<th>(1000/T)</th>
<th>(\log R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>159</td>
<td>357.1</td>
<td>45</td>
<td>0.391</td>
<td>1.44</td>
<td>58.7</td>
<td>50.5</td>
<td>21.1</td>
<td>2.80</td>
<td>1.324</td>
</tr>
<tr>
<td>137</td>
<td>357.1</td>
<td>45</td>
<td>0.586</td>
<td>1.66</td>
<td>65.9</td>
<td>29.1</td>
<td>20.9</td>
<td>2.80</td>
<td>1.320</td>
</tr>
<tr>
<td>160</td>
<td>357.1</td>
<td>180</td>
<td>0.506</td>
<td>1.86</td>
<td>64.9</td>
<td>38.1</td>
<td>20.8</td>
<td>2.80</td>
<td>1.318</td>
</tr>
<tr>
<td>111</td>
<td>370.5</td>
<td>90</td>
<td>0.724</td>
<td>0.766</td>
<td>99.2</td>
<td>21.2</td>
<td>29.8</td>
<td>2.70</td>
<td>1.474</td>
</tr>
<tr>
<td>133</td>
<td>384.5</td>
<td>60</td>
<td>0.415</td>
<td>1.89</td>
<td>117</td>
<td>50.1</td>
<td>39.9</td>
<td>2.60</td>
<td>1.601</td>
</tr>
<tr>
<td>136</td>
<td>400.0</td>
<td>45</td>
<td>0.551</td>
<td>1.56</td>
<td>178</td>
<td>39.6</td>
<td>51.3</td>
<td>2.50</td>
<td>1.710</td>
</tr>
<tr>
<td>135</td>
<td>400.0</td>
<td>60</td>
<td>0.276</td>
<td>1.26</td>
<td>120</td>
<td>67.4</td>
<td>53.2</td>
<td>2.50</td>
<td>1.726</td>
</tr>
<tr>
<td>114</td>
<td>416.6</td>
<td>45</td>
<td>0.980</td>
<td>0.977</td>
<td>227</td>
<td>10.1</td>
<td>72.7</td>
<td>2.40</td>
<td>1.862</td>
</tr>
<tr>
<td>121</td>
<td>416.6</td>
<td>90</td>
<td>1.27</td>
<td>0.570</td>
<td>176</td>
<td>5.10</td>
<td>61.4</td>
<td>2.40</td>
<td>1.788</td>
</tr>
<tr>
<td>134</td>
<td>434.6</td>
<td>45</td>
<td>0.371</td>
<td>1.69</td>
<td>315</td>
<td>63.8</td>
<td>106</td>
<td>2.30</td>
<td>2.025</td>
</tr>
<tr>
<td>158</td>
<td>434.8</td>
<td>45</td>
<td>0.318</td>
<td>1.17</td>
<td>262</td>
<td>71.0</td>
<td>98.0</td>
<td>2.30</td>
<td>1.991</td>
</tr>
<tr>
<td>138</td>
<td>434.9</td>
<td>60</td>
<td>0.450</td>
<td>1.27</td>
<td>279</td>
<td>39.7</td>
<td>98.4</td>
<td>2.30</td>
<td>1.993</td>
</tr>
</tbody>
</table>

\(C_4H_{10}\) and HFA are in \(10^{-6}\) mole cm\(^{-3}\)

\(CF_3H\) and \(C_2F_6\) are in \(10^{-12}\) mole cm\(^{-3}\) sec\(^{-1}\)
### TABLE 10

Photolysis of TFMI in the Presence of n-BUTANE

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>C₄H₁₀</th>
<th>CF₃I</th>
<th>CF₃H</th>
<th>C₂F₆</th>
<th>R</th>
<th>1000/T</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>141</td>
<td>357.1</td>
<td>450</td>
<td>1.419</td>
<td>1.58</td>
<td>7.78</td>
<td>1.27</td>
<td>16.5</td>
<td>2.80</td>
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<td>142</td>
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<td>13.4</td>
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<td>16.8</td>
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<td>450</td>
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<td>1.22</td>
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<td>450</td>
<td>1.439</td>
<td>1.65</td>
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<td>25.7</td>
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<tr>
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<td>1.65</td>
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<td>1.07</td>
<td>30.7</td>
<td>2.50</td>
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<td>125</td>
<td>416.4</td>
<td>450</td>
<td>1.145</td>
<td>1.79</td>
<td>11.2</td>
<td>3.56</td>
<td>41.4</td>
<td>2.40</td>
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<tr>
<td>113</td>
<td>416.6</td>
<td>180</td>
<td>1.775</td>
<td>1.75</td>
<td>41.9</td>
<td>1.75</td>
<td>40.9</td>
<td>2.40</td>
<td>1.612</td>
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<tr>
<td>116</td>
<td>416.7</td>
<td>200</td>
<td>1.628</td>
<td>1.29</td>
<td>34.5</td>
<td>1.75</td>
<td>41.6</td>
<td>2.40</td>
<td>1.619</td>
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<tr>
<td>139</td>
<td>434.8</td>
<td>300</td>
<td>1.410</td>
<td>1.51</td>
<td>30.3</td>
<td>1.41</td>
<td>62.3</td>
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<tr>
<td>144</td>
<td>434.9</td>
<td>450</td>
<td>1.315</td>
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<td>18.4</td>
<td>0.804</td>
<td>65.1</td>
<td>2.30</td>
<td>1.814</td>
</tr>
</tbody>
</table>

C₄H₁₀ and CF₃I are in 10⁻⁶ mole cm⁻³
CF₃H and C₂F₆ are in 10⁻¹² mole cm⁻³ sec⁻¹
This may be interpreted in terms of the following reactions:

\[
\begin{align*}
\text{CF}_3\text{H} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot & \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{CF}_3\text{H} \\
\text{CF}_3\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{CF}_3\text{H} \\
\text{CF}_3\text{H} + \text{CH}_3\text{CH}_2\text{CHCH}_3 & \rightarrow \text{CH}_3\text{CH}=\text{CHCH}_3 + \text{CF}_3\text{H}
\end{align*}
\]

(cis or trans)

The reaction \( \text{C}_4\text{H}_8 + \text{CF}_3\cdot \rightarrow \text{C}_4\text{H}_7\text{CF}_3^+ \) may also be of importance, particularly where an allylic hydrogen atom is involved. When TFMII is used as radical source, butene formation is inhibited, presumably by the reactions:

\[
\begin{align*}
\text{C}_4\text{H}_9^+ + \text{I}^- & \rightarrow \text{C}_4\text{H}_9\text{I} \\
\text{C}_4\text{H}_9^+ + \text{I}_2 & \rightarrow \text{C}_4\text{H}_9\text{I} + \text{I}^-
\end{align*}
\]

In consequence the additional sources of fluoroform indicated in the above reaction scheme are removed when CF\(_3\)I is used, leading to the observed difference in rate constants. It is evident that if every alkyl radical formed by abstraction lost a further hydrogen atom to form the corresponding olefin, rate constants calculated using
the total yield of fluoroform would be high by a factor of 2, but the activation energy would be unaffected. As will be seen from Tables 9 and 10, the observed factor for butane is around 1.4, indicating that the cross-disproportion/combination ratio for C\textsubscript{4}H\textsubscript{9}\textsuperscript{·} and CF\textsubscript{3}\textsuperscript{·} is less than 1, while for cyclohexane (Tables 7 and 8) the ratio is around 2.7, which suggests further abstraction from cyclohexene. In neither case is the activation energy appreciably altered. It seems likely that most of the reported rate constants for hydrogen atom abstraction from alkanes using HFA (and presumably HFAM) will be high, but that the reported Arrhenius parameters are unlikely to be seriously affected. In systems where there is only one hydrogen atom in the substrate molecule, further reactions of the above type are not possible. Accordingly HFA was used as radical source only with the perfluoroaldehydes, TFMI being used in all other cases.

If direct abstraction from the hydrogen substrate RH is the only source of fluoroform, then,

\[ R = \frac{k_a}{k_c} = \frac{R_{\text{CF}_3\text{H}}}{R_{\text{C}_2\text{F}_6}[\text{RH}]} \]

Thus a plot of \( \frac{1}{R_{\text{C}_2\text{F}_6}} \) against \([\text{RH}] / R_{\text{CF}_3\text{H}}\) should be linear, passing through the origin. As will be seen from Figs. 7 and 8 this is in fact found to be the case for n-butane and cyclohexane using TFMI as radical source. The gradient of these plots corresponds to the mean value of R at the temperature chosen.
FIG. 7.

$$\frac{10^{-6}}{R_{C_2F_6}}$$

10^{-6}[C_6H_{12}] / R_{CF_3H} \times 10^3 \text{ at } 161.6^\circ C$

TFMI + CYCLOHEXANE

FIG. 8.

$$\frac{10^{-6}}{R_{C_2F_6}}$$

10^{-6}[C_4H_{10}] / R_{CF_3H}$

O at 143.4^\circ C

○ at 97.2^\circ C

TFMI + n-BUTANE
As a further test of mechanism it may be verified that R is independent of run time (demonstrating that attack on products is unimportant), and of the relative concentrations of reactants. Whenever possible a ten-fold or greater variation in make-up and run time was used for each system studied. The available kinetic data for the reactions

\[
\begin{align*}
\text{n-CH}_4\text{H}_{10} + \text{CF}_3\cdot & \rightarrow \text{CH}_4\text{H}_9\cdot + \text{CF}_3\text{H} \quad \text{and} \\
\text{cyclo-CH}_6\text{H}_{12} + \text{CF}_3\cdot & \rightarrow \text{CH}_6\text{H}_{11}\cdot + \text{CF}_3\text{H}
\end{align*}
\]

are summarised in Table II below.

It is convenient to compare rate constants at 164°C, since at this temperature 2·303RT = 2,000, and hence:

\[
\log k_{164} = \log A - \frac{E}{2} \quad (E \text{ is in kcal/mole})
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E (kcal/mol)</th>
<th>log A</th>
<th>log k_{164}</th>
<th>Source</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>5·74 ± 28</td>
<td>11·31 ± 16</td>
<td>8·4</td>
<td>TFMI</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>6·19 ± 43</td>
<td>11·77 ± 24</td>
<td>8·7</td>
<td>HFA</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>5·1</td>
<td>11·15</td>
<td>8·6</td>
<td>HFA</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>5·3</td>
<td>11·46</td>
<td>8·8</td>
<td>HPAM*</td>
<td>60</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6·39 ± 28</td>
<td>12·16 ± 16</td>
<td>9·0</td>
<td>TFMI</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>6·2</td>
<td>12·5</td>
<td>9·4</td>
<td>HFA</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>5·00</td>
<td>11·44</td>
<td>8·9</td>
<td>HFA</td>
<td>62</td>
</tr>
</tbody>
</table>

E is in kcal/mole, A and k_{164} in mole\(^{-1}\)cm\(^{-3}\)sec\(^{-1}\).

* Competitive study using CF\(_3\)\cdot + D\(_2\) → CF\(_3\)D + D\(_{\cdot}\) as reference reaction.
Comparison with the corresponding parameters for methyl radicals (Table 12) shows the expected activation energy difference of around 3 kcal/mole, with little change in log A. In both cases log $k_{164}$ is greater by 1.3 for trifluoromethyl radicals. At this temperature, therefore, abstraction of a secondary hydrogen atom from an alkane by CF$_3^-$ is about 20 times more rapid than the corresponding abstraction by CH$_3^-$.

**TABLE 12**

<table>
<thead>
<tr>
<th>TRIFLUOROMETHYL</th>
<th>METHYL RADICALS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
</tr>
<tr>
<td>n-Butane</td>
<td>5.7</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.4</td>
</tr>
</tbody>
</table>

*CD$_3$ Radicals  E is in kcal/mole, A and $k_{164}$ in mole$^{-1}$ cm$^3$ sec$^{-1}$

It is possible that the presence of iodine in the system may affect the reaction scheme other than by removal of alkyl radicals. However, inhibition of butene formation when CF$_3$I is used indicates that the reactions

$$I^- + C_4H_9^+ \rightarrow HI + C_4H_8$$

$$\rightarrow$$

$$CF_3^- \rightarrow CF_3H + I^-$$

do not occur to any appreciable extent. Reactions of the type: $RH + I^- \rightarrow R^- + HI$

are also unlikely to be important, having far higher activation energies than the corresponding reactions of CF$_3^-$ e.g.

$$CF_3^- + C_3H_8 \rightarrow CF_3H + C_3H_7^-$$

$$E | log A | log $k_{164}$ | Ref. |
| 6.2 | 11.7 | 8.6 | 60   |

$$I^- + C_3H_8 \rightarrow HI + C_3H_7^-$$

$$E | log A | log $k_{164}$ | Ref. |
| 25.0 | 17.2 | 4.7 | 95   |
If hydrogen abstraction by iodine atoms did lead to the formation of appreciable amounts of fluoroform, then higher activation energy values would be expected, using TFMI. This is not the case, as will be seen from Figs. 5 and 6. The following simple reaction scheme is therefore proposed:

\[
\begin{align*}
\text{CF}_3\text{I} & \xrightleftharpoons{\text{hv}} \text{CF}_3\cdot + \text{I}^- \\
& \xrightarrow{\text{RH}} \text{CF}_3\text{H} + \text{R}\cdot \xrightarrow{\text{I}_2} \text{RI} + \text{I}^-. 
\end{align*}
\]

This mechanism cannot, of course, be applied uncritically to systems where RH is not a hydrocarbon. In each case therefore, the mechanism was tested by studying the effect on \( R \) of variations in run time, make-up, and \( \text{CF}_3\cdot \) concentration.

In the course of this work, hydrogen abstraction by methyl radicals from a number of substrates has also been studied. Azomethane is a convenient and widely used photolytic source of methyl radicals. Its decomposition takes place by the following mechanism:

\[
\begin{align*}
\text{CH}_3\text{N}_2\text{CH}_3 + \text{hv} & \rightarrow 2\text{CH}_3\cdot + \text{N}_2 \\
\text{CH}_3\cdot + \text{CH}_3\cdot & \rightarrow \text{C}_2\text{H}_6 \quad (k_c) \\
\text{CH}_3\cdot + \text{CH}_3\text{N}_2\text{CH}_3 & \rightarrow \text{CH}_4 + \text{CH}_3\text{N}_2\text{CH}_2\cdot \quad (k_a) \\
\text{CH}_3\cdot + \text{CH}_3\text{N}_2\text{CH}_3 & \rightarrow (\text{CH}_3)_2\text{N}_2\text{CH}_3 \xrightarrow{\text{CH}_3\cdot} (\text{CH}_3)_2\text{N}_2(\text{CH}_3)_2
\end{align*}
\]
### TABLE 13.

**AZOMETHANE PHOTOLYSIS**

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>AZO</th>
<th>N₂</th>
<th>C₂H₆</th>
<th>CH₄</th>
<th>R</th>
<th>1,000/T</th>
<th>log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>493</td>
<td>526.3</td>
<td>135</td>
<td>1.84</td>
<td>395</td>
<td>48.4</td>
<td>223</td>
<td>17.4</td>
<td>1.90</td>
<td>1.241</td>
</tr>
<tr>
<td>503</td>
<td>526.3</td>
<td>135</td>
<td>0.741</td>
<td>186</td>
<td>41.7</td>
<td>95.1</td>
<td>19.9</td>
<td>1.90</td>
<td>1.298</td>
</tr>
<tr>
<td>498</td>
<td>344.8</td>
<td>135</td>
<td>7.62</td>
<td>579</td>
<td>412</td>
<td>63.1</td>
<td>.408</td>
<td>2.90</td>
<td>1.611</td>
</tr>
<tr>
<td>500</td>
<td>344.8</td>
<td>450</td>
<td>2.74</td>
<td>275</td>
<td>237</td>
<td>19.2</td>
<td>.455</td>
<td>2.90</td>
<td>1.658</td>
</tr>
<tr>
<td>501</td>
<td>344.8</td>
<td>45</td>
<td>1.37</td>
<td>165</td>
<td>163</td>
<td>6.44</td>
<td>.367</td>
<td>2.90</td>
<td>1.565</td>
</tr>
</tbody>
</table>

The azomethane concentration, AZO, is in $10^{-6}$ mole cm$^{-3}$

$N₂$, $C₂H₆$ and $CH₄$ are in $10^{-12}$ mole cm$^{-3}$ sec$^{-1}$

Mean R at 526.3°K = 18.7  \[ \therefore \log R_{526.3} = 1.272 \]

Mean R at 344.8°K = 1410  \[ \therefore \log R_{344.8} = 1.613 \]

\[ \therefore \text{Gradient of Arrhenius Plot} = (1.272 - 1.613)/(1.9 - 2.9) = -1.659 \]

\[ \therefore \text{Intercept on Log R axis} = 1.272 + 1.9 (1.659) = 4.424 \]

\[ \therefore \log A = 4.42 + 6.68 = 11.10 \]

\[ E = 2.303R \times 1.659 = 7.59 \text{ kcal/mole.} \]
Taking the quantum yield of nitrogen as unity, that for ethane formed by intramolecular elimination is about 0.007 (6) and the total yield of ethane must be corrected for this before calculating the \( \text{CH}_3^\cdot \) concentration. In the above scheme \( k_a \) is high, and abstraction from the radical source makes a large contribution to the total yield of methane for most hydrogen substrates. Accordingly the photolysis was studied briefly to provide internally consistent correction factors (Table 13), the Arrhenius parameters obtained being in agreement with those of previous workers (Table 14).

<table>
<thead>
<tr>
<th>( \text{CH}_3^\cdot + \text{CH}_3\text{N}_2\text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_3\text{N}_2\text{CH}_2^\cdot )</th>
<th>( E ) (kcal/mole)</th>
<th>( \log A )</th>
<th>( \log k_{164} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>11.1</td>
<td>7.3</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>7.9</td>
<td>11.0</td>
<td>7.0</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>8.7</td>
<td>11.5</td>
<td>7.1</td>
<td>97</td>
<td></td>
</tr>
</tbody>
</table>

\( E \) is in kcal/mole, \( A \) and \( k_{164} \) in mole\(^{-1}\)cm\(^3\)sec\(^{-1}\) (109)

In investigating hydrogen atom abstraction from perfluoroaldehydes by methyl radicals, di-tertiary-butyl peroxide (DTBP) was used. Being a thermal source, photolysis of the aldehydes was eliminated. \( k_a \) for DTBP is considerably lower than for \( \text{R}_n\text{CHO} \), and abstraction from the radical source made little contribution to the methane formed. Accordingly the photolysis of DTBP was not studied, established parameters for the following reaction being used. \( (\text{CH}_3)_3\text{O}_2(\text{CH}_3)_3 + \text{CH}_3^\cdot \rightarrow \text{CH}_4 + (\text{CH}_3)_3\text{O}_2(\text{CH}_3)_2\text{CH}_2^\cdot \)

\( E = 11.9 \) kcal/mole, \( \log A = 12.7 \) (A is in mole\(^{-1}\)cm\(^3\)sec\(^{-1}\)) (109)
Photolysis or thermal decomposition of the esters of azodiformic acid would at first sight appear to offer a useful source of alkyl and alkoxy carbonyl radicals.

\[
\begin{align*}
\text{ROCN} & \rightarrow N_2 + 2 \cdot \text{C} \xrightarrow{200^\circ} 2R^\cdot \\
\text{RO} & \text{CO}_2 + \text{N}_2
\end{align*}
\]

If the above reaction scheme is obeyed then: \( \frac{\text{CO}_2}{N_2} = 2 \) and \( \sum R^\cdot/\text{CO}_2 = 1 \)

Jones and Thynne studied the gas-phase thermal decomposition of Dimethyl Azodiformate at 162°C and found ratios of about 0.94 and 0.06 respectively. Thus less than half the methoxycarbonyl radicals formed decomposed, while auto-combination accounts for as little as 6% of the methyl radicals formed (no methane being detected). In the present work this discrepancy between observed and predicted ratios was investigated by analysis of the products formed on photolysing M/100 solutions of dimethylazodiformate in dodecane. Under these conditions the characteristic red colour of the ester disappeared rapidly, although the yield of nitrogen indicated less than 10% decomposition, the solution becoming a viscous gel. On pumping off the solvent, and extracting with dimethylformamide (DMF), a semi-solid polymer-like substance remained, which contained:

- 44.1% CARBON,
- 12.6% NITROGEN,
- 6.4% HYDROGEN.

and 36.8% OXYGEN (by difference).

The mean molecular weight was determined using a MECHROLAB Vapour Pressure Osmometer. Solutions ranging from
50 to 4 g/l were made up with DMF as solvent and Benzil solutions of comparable strength were used to calibrate the instrument. The molecular weight was found to be 520 ± 50, the error limit representing the spread of results from several determinations on different polymer samples.

These results may be interpreted in terms of addition of methyl and methoxycarbonyl radicals to the azo linkage, followed by a isomerisation:

\[
R' + \text{MeO}^\cdot \rightarrow \text{MeO}^\cdot \rightarrow R
\]

The radical thus formed may then react by further addition to the azodiformate. The observed molecular weight suggests an average of about three azodiformate units per polymer molecules. The low nitrogen yield and rapid bleaching are both explained by this mechanism, while it is evident that most of the methyl, and about half the methoxycarbonyl, radicals formed react by addition. The decomposition of azodiformate esters is not, therefore, likely to prove useful as a radical source.
CHAPTER 4.

When this work was started, virtually no quantitative kinetic data had been reported for free-radical reactions involving silicon compounds (101). The reactions of silanes, which in many respects are analogous to those of hydrocarbons, often occur with greater violence or under milder conditions. For example the oxidation of silane

\[
\text{SiH}_4 + 2\text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}
\]

occurs spontaneously at room temperature. Although the mechanism of combustion reactions has yet to be established unequivocally, it is generally agreed that the initial attack takes the form of a hydrogen abstraction, probably by HO_2^-.

\[
e.g. \text{CH}_4 + \text{HO}_2^- \rightarrow \text{CH}_3^- + \text{H}_2\text{O}_2
\]

This suggests that the activation energy for hydrogen abstraction from silanes is lower than that for hydrocarbons, indicating the Si-H bond strength to be less than that of a C-H bond in a similar molecule environment. The first systematic study of hydrogen abstraction from molecules containing silicon was made by Kerr and his co-workers (98, 99) who reacted methyl radicals with a number of substituted silanes. Their results are summarised in Table 15. These results suggest that the observed high rates of reaction are due, not to low activation energies, but to high A-factors, which the authors attributed to ionic complex formation during the transition state.
TABLE 15.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E$ (kcal/mole)</th>
<th>$\log A$</th>
<th>$\log k_{164}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3^\cdot + \text{F}_3\text{SiH} \rightarrow \text{CH}_4 + \text{F}_3\text{Si}^\cdot$</td>
<td>8.7</td>
<td>12.4</td>
<td>8.0</td>
</tr>
<tr>
<td>$\text{CH}_3^\cdot + \text{Cl}_3\text{SiH} \rightarrow \text{CH}_4 + \text{Cl}_3\text{Si}^\cdot$</td>
<td>8.5</td>
<td>13.4</td>
<td>9.1</td>
</tr>
<tr>
<td>$\text{CH}_3^\cdot + \text{MeCl}_2\text{SiH} \rightarrow \text{CH}_4 + \text{MeCl}_2\text{Si}^\cdot$</td>
<td>7.2</td>
<td>12.9</td>
<td>9.3</td>
</tr>
<tr>
<td>$\text{CH}_3^\cdot + \text{Me}_3\text{SiH} \rightarrow \text{CH}_4 + \text{Me}_3\text{Si}^\cdot$</td>
<td>7.0</td>
<td>11.1</td>
<td>7.6</td>
</tr>
<tr>
<td>$\text{CH}_3^\cdot + \text{ClSiMe}_3 \rightarrow \text{CH}_4 + \text{ClSiMe}_2\text{CH}_2^\cdot$</td>
<td>11.5</td>
<td>13.4</td>
<td>7.6</td>
</tr>
<tr>
<td>$\text{CH}_3^\cdot + \text{Cl}_2\text{SiMe}_2 \rightarrow \text{CH}_4 + \text{Cl}_2\text{SiMeCH}_2^\cdot$</td>
<td>11.6</td>
<td>13.2</td>
<td>7.4</td>
</tr>
<tr>
<td>$\text{CH}_3^\cdot + \text{Cl}_3\text{SiMe} \rightarrow \text{CH}_4 + \text{Cl}_3\text{SiCH}_2^\cdot$</td>
<td>11.5</td>
<td>12.9</td>
<td>7.1</td>
</tr>
</tbody>
</table>

$E$ is in kcal/mole, $A$ and $k_{164}$ in mole$^{-1}$cm$^3$sec$^{-1}$.

In a recent re-investigation of hydrogen abstraction from trichlorosilane, however, Kerr (103) obtained the following Arrhenius parameters:

$$E = 4.3 \text{ kcal/mole}, \quad \log A = 10.8,$$

the activation energy being almost half that previously reported. In Fig. 9 the results of these two studies are shown as a single Arrhenius plot, which appears to exhibit distinct curvature. It seems, therefore, that in the case of the halosilanes, the reaction mechanism may be more complex than suspected, and that little confidence should be placed in the high A-factors reported.

In the present work the reactions of methyl and trifluoromethyl radicals with silane, trimethylsilane and tetramethylsilane have been studied: the results are recorded in tables 16 to 21 and presented graphically in Figs. 10 to 14. Since the beginning of this year (1969) a considerable quantity of kinetic data has become available for the abstraction of hydrogen from group IV tetramethyls. This is summarised in Table 22.
REPORTED Arrhenius Parameters for the Reaction: 

\[ \text{CF}_3^+ + \text{Cl}_3\text{SiH} \rightarrow \text{CF}_2\text{H} + \text{Cl}_3\text{Si}^+ \]

BLACK CIRCLES indicate the results of Kerr, Stephens and Young (103).

VERTICAL BARS show the range of values obtained at each of five temperatures by Kerr, Slater and Young (98).
<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>AZO</th>
<th>SILANE</th>
<th>N₂</th>
<th>C₂H₆</th>
<th>CH₄⁺</th>
<th>CH₄⁻</th>
<th>R</th>
<th>1000/T</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
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<td>2·70</td>
<td>2·734</td>
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<td>450</td>
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<td>14·5</td>
<td>9·91</td>
<td>0·69</td>
<td>1·75</td>
<td>0·147</td>
<td>2·50</td>
<td>1·167</td>
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<td>135</td>
<td>0·104</td>
<td>3·33</td>
<td>14·0</td>
<td>8·11</td>
<td>1·18</td>
<td>5·03</td>
<td>0·535</td>
<td>2·30</td>
<td>1·728</td>
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<td>18·5</td>
<td>12·0</td>
<td>33·8</td>
<td>1·55</td>
<td>2·10</td>
<td>0·191</td>
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<td>0·145</td>
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<td>30·6</td>
<td>2·03</td>
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<td>3·42</td>
<td>1·90</td>
<td>0·535</td>
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<tr>
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<td>135</td>
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<td>2·27</td>
<td>2·4</td>
<td>13·0</td>
<td>3·23</td>
<td>1·90</td>
<td>0·509</td>
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<tr>
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<td>181</td>
<td>117</td>
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<td>65·1</td>
<td>2·99</td>
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<td>334</td>
<td>261</td>
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<td>0·758</td>
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<td>1·045</td>
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<td>0·224</td>
<td>291</td>
<td>114</td>
<td>52</td>
<td>62</td>
<td>24·6</td>
<td>2·50</td>
<td>1·392</td>
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<td>584</td>
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<td>450</td>
<td>1·64</td>
<td>1·66</td>
<td>193</td>
<td>11·2</td>
<td>21</td>
<td>214</td>
<td>41·2</td>
<td>2·30</td>
<td>1·614</td>
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<td>585</td>
<td>476·2</td>
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<td>1·31</td>
<td>222</td>
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<td>21</td>
<td>224</td>
<td>90·6</td>
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<td>1·962</td>
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<td>476·2</td>
<td>225</td>
<td>2·86</td>
<td>0·255</td>
<td>346</td>
<td>27·0</td>
<td>129</td>
<td>133</td>
<td>100</td>
<td>2·10</td>
<td>2·017</td>
</tr>
</tbody>
</table>

**TABLE 16**

\( \text{Me}_4 \text{Si} + \text{CH}_3^· \)

**TABLE 17**

\( \text{SiH}_4^+ + \text{CH}_3^· \)

(Units under)

(Table 18)

(63)
### TABLE 18

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>AZO</th>
<th>SILANE</th>
<th>(N_2)</th>
<th>(C_2H_6)</th>
<th>(CH_4) (AZO)</th>
<th>(CH_4) (SILANE)</th>
<th>(\frac{1000}{T})</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
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<td>0.115</td>
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<td>22.7</td>
<td>25.6</td>
<td>0.23</td>
<td>3.44</td>
<td>551</td>
<td>2.90</td>
</tr>
<tr>
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<td>370.4</td>
<td>135</td>
<td>0.236</td>
<td>2.54</td>
<td>43.0</td>
<td>31.8</td>
<td>1.2</td>
<td>14.8</td>
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<td>2.70</td>
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<td>0.497</td>
<td>1.73</td>
<td>70.7</td>
<td>56.1</td>
<td>3.3</td>
<td>15.2</td>
<td>1.17</td>
<td>2.70</td>
</tr>
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<td>135</td>
<td>1.01</td>
<td>1.02</td>
<td>127</td>
<td>102</td>
<td>9.1</td>
<td>11.2</td>
<td>1.09</td>
<td>2.70</td>
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<td>89.3</td>
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<td>7.8</td>
<td>38.6</td>
<td>2.70</td>
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<td>1.32</td>
<td>59.0</td>
<td>29.0</td>
<td>8.1</td>
<td>36.7</td>
<td>5.17</td>
<td>2.30</td>
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<td>32.6</td>
<td>3.72</td>
<td>1.8</td>
<td>39.2</td>
<td>13.0</td>
<td>2.10</td>
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<td>153</td>
<td>20.1</td>
<td>39</td>
<td>117</td>
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<td>0.500</td>
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<td>99.2</td>
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<td>69.8</td>
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<td>1.18</td>
<td>34.0</td>
<td>2.24</td>
<td>3.0</td>
<td>46.5</td>
<td>28.0</td>
<td>1.90</td>
</tr>
</tbody>
</table>

The concentrations, AZO and SILANE, are in \(10^{-6}\) mole cm\(^{-3}\), the rates of formation of nitrogen, ethane and methane (formed by abstraction from azomethane or from the silane) are given in \(10^{-12}\) mole cm\(^{-3}\) sec\(^{-1}\).
### TABLE 19

Photolysis of TFMI in the Presence of Silane

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>S</th>
<th>CF&lt;sub&gt;3&lt;/sub&gt;H</th>
<th>CF&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;6&lt;/sub&gt;</th>
<th>R</th>
<th>1000</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>592</td>
<td>312.5</td>
<td>450</td>
<td>1.00</td>
<td>1.01</td>
<td>37.0</td>
<td>0.651</td>
<td>40.5</td>
<td>3.20</td>
</tr>
<tr>
<td>604</td>
<td>327.9</td>
<td>3600</td>
<td>0.674</td>
<td>0.687</td>
<td>12.9</td>
<td>0.065</td>
<td>77.7</td>
<td>3.05</td>
</tr>
<tr>
<td>601</td>
<td>344.8</td>
<td>4500</td>
<td>0.159</td>
<td>2.03</td>
<td>5.97</td>
<td>0.198</td>
<td>92.2</td>
<td>2.90</td>
</tr>
<tr>
<td>594</td>
<td>344.8</td>
<td>900</td>
<td>0.557</td>
<td>0.565</td>
<td>16.9</td>
<td>0.110</td>
<td>92.8</td>
<td>2.90</td>
</tr>
<tr>
<td>595</td>
<td>344.8</td>
<td>900</td>
<td>0.372</td>
<td>1.40</td>
<td>38.9</td>
<td>0.981</td>
<td>111.0</td>
<td>2.90</td>
</tr>
<tr>
<td>603</td>
<td>370.4</td>
<td>3600</td>
<td>0.521</td>
<td>0.532</td>
<td>23.6</td>
<td>0.084</td>
<td>171.0</td>
<td>2.70</td>
</tr>
<tr>
<td>596</td>
<td>400.0</td>
<td>900</td>
<td>0.311</td>
<td>1.17</td>
<td>82.6</td>
<td>1.33</td>
<td>262.0</td>
<td>2.50</td>
</tr>
</tbody>
</table>

### TABLE 20

Photolysis of TFMI in the Presence of Trimethylsilane

<table>
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<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>TMSH</th>
<th>CF&lt;sub&gt;3&lt;/sub&gt;H</th>
<th>CF&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;6&lt;/sub&gt;</th>
<th>R</th>
<th>1000</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>530</td>
<td>322.6</td>
<td>150</td>
<td>0.650</td>
<td>2.06</td>
<td>57.9</td>
<td>1.80</td>
<td>66.9</td>
<td>3.10</td>
</tr>
<tr>
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<td>344.8</td>
<td>150</td>
<td>0.991</td>
<td>0.936</td>
<td>108.0</td>
<td>0.98</td>
<td>110.0</td>
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<tr>
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<td>344.8</td>
<td>150</td>
<td>0.247</td>
<td>2.21</td>
<td>43.2</td>
<td>2.14</td>
<td>121.0</td>
<td>2.90</td>
</tr>
<tr>
<td>532</td>
<td>370.4</td>
<td>650</td>
<td>0.564</td>
<td>1.79</td>
<td>136.0</td>
<td>1.44</td>
<td>218.0</td>
<td>2.70</td>
</tr>
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<td>45</td>
<td>0.284</td>
<td>2.54</td>
<td>183.0</td>
<td>8.20</td>
<td>228.0</td>
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<tr>
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<td>479.0</td>
<td>3.69</td>
<td>1210.0</td>
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</table>

Concentration of silane, S, trimethylsilane, TMSH, and TFMI are in $10^{-6}$ mole cm$^{-3}$, CF<sub>3</sub>H and CF<sub>2</sub>F<sub>6</sub> are in $10^{-12}$ mole cm$^{-3}$ sec$^{-1}$. 
TABLE 21
Photolysis of TFMI in the Presence of Tetramethysilane

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>TMS</th>
<th>TFMI</th>
<th>CF₃H</th>
<th>C₂F₆</th>
<th>R</th>
<th>1000/T</th>
<th>Log R</th>
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<td>1800</td>
<td>0.250</td>
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<td>0.663</td>
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<td>1.29</td>
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<td>0.365</td>
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<td>1.22</td>
<td>16.7</td>
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<tr>
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<td>0.251</td>
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<td>11.4</td>
<td>0.686</td>
<td>58.0</td>
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<td>1.763</td>
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<td>1.33</td>
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<td>1.68</td>
<td>156</td>
<td>1.90</td>
<td>2.193</td>
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</table>

Concentration of tetramethysilane, TMS, and TFMI in 10⁻⁶ mole cm⁻³,
CF₃H and C₂F₆ in 10⁻¹² mole cm⁻³ sec⁻¹.
FIG. 10. HYDROGEN ABSTRACTION FROM SILANE

NOTE: Since the completion of the text of this Thesis, Arrhenius Parameters have been reported for the methyl radical reaction, which are in excellent agreement with those obtained in the present work.

Ref 155: $E = 7.0 \pm 0.6$  $\log A = 11.8 \pm 0.3$

This work: $E = 6.9 \pm 0.2$  $\log A = 11.8 \pm 1$
FIG. 11.

HYDROGEN ATOM ABSTRACTION BY CF$_3$. AND CH$_3$. FROM
TRIMETHYLSILANE AND TETRAMETHYLSILANE

- ABSTRACTION FROM Me$_3$SiH
- ABSTRACTION FROM Me$_4$Si

1,000/T

Log R

- 3.0
- 2.0
- 1.0
- 0.0
- 1.0
- 2.0

1.9  2.1  2.3  2.5  2.7  2.9  3.1
FIG. 12.

CF_3- AND CH_3 ATTACK ON SILANE
TEST OF MECHANISM

\[ 10^{-6} \frac{[\text{SiH}_4]}{R_{\text{Rad H}}} \]

\[ \text{SiH}_4 + \text{Rad} \rightarrow \text{SiH}_3^\cdot + \text{RadH} \]

- \( \text{Rad} = \text{CF}_3^\cdot \) at 71.6°C (1000/T = 2.90)
- \( \text{Rad} = \text{CH}_3^\cdot \) at 71.6°C.
FIG. 13.

CF₃- and CH₃- ATTACK ON TRIMETHYLSILANE
TEST OF MECHANISM

\[
\begin{align*}
10^{-6} \frac{[Me_3SiH]}{R_{RadH}} & \quad 10^{-6} \frac{C_2F_6}{R_{C_2H}} \\
0.0 & \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0
\end{align*}
\]

\[
Me_3SiH + Rad \rightarrow Me_3Si^+ + RadH \quad \text{Temp.} = 97.2
\]

\( \bullet \) Rad = CH₃; \( \bigcirc \) Rad = CF₃; \( \text{1000/T = 2.70} \)

Allowance is made for the reaction:

\[
Rad^+ + (CH₃)₃SiH \rightarrow (CH₃)₂SiHCH₂^+ + RadH \quad (k_{TRI})
\]

by assuming \( k_{TRI} = k_{TETRA} \).

\[
Rad^+ + (CH₃)₄Si \rightarrow (CH₃)₃SiCH₂^+ + RadH \quad (k_{TETRA})
\]
PHOTOLYSIS OF TFMI IN THE PRESENCE OF TETRAMETHYSILANE.

\[
(\text{CH}_3)_4\text{Si} + \text{CF}_3 \cdot \rightarrow (\text{CH}_3)_3\text{SiCH}_2 \cdot + \text{CF}_3\text{H}
\]

\[10^{-6}/R_{\text{C}_2\text{F}_6}^3\]

\[\circ [\text{Me}_4\text{Si}] / R_{\text{CF}_3\text{H}}\]

O At 97.2°C: \([\text{Me}_4\text{Si}] / R_{\text{CF}_3\text{H}}\) is in \(10^5\) secs.

O At 203°C: " " " " " \(10^4\) "

FIG. 14.

TEST OF MECHANISM

The co-incidence of the two sets of points arises from the fact that:
\[R_{203} \approx 10 \times R_{97}\]
The results of Kerr and his co-workers (98) for abstraction from Me₄Si by both CH₃· and CF₃· are in excellent agreement with those obtained in the present work, and within experimental error are identical with those reported for neopentane. i.e.

\[
\text{CH}_3 + \text{M(CH}_3)_4 \rightarrow \text{CH}_4 + \text{M(CH}_3)_3\text{CH}_2. \quad E = 10.2 \pm 0.2\text{kcal/mole; Log } A = 11.5 \pm 0.2
\]

\[
\text{CF}_3 + \text{M(CH}_3)_4 \rightarrow \text{CF}_3\text{H} + \text{M(CH}_3)_3\text{CH}_2. \quad E = 7.4 \pm 0.2\text{kcal/mole; Log } A = 11.9 \pm 1
\]

\(M = C \text{ or Si}\)

The difference of around 2.8 kcal in the activation energy requirements for CH₃· and CF₃· is in accord with that reported for hydrocarbon systems (77). It is evident that the substitution of silicon for carbon as central atom has little effect on the kinetics of abstraction from the methyl groups. This is in disagreement with the findings of Chaudry and Gowenlock (104) who observed a marked lowering in both \(E\) and \(A\) for abstraction of hydrogen by CH₃· on going from Me₄Si to Me₄Pb. The parameters reported by these workers for tetramethylsilane differ from those obtained in the present work, and by Kerr and his co-workers, by an amount considerably outwith experimental error. The reason for this discrepancy is not clear.

Arrhenius parameters for abstraction reactions in which a silicon-hydrogen bond is severed are recorded in Table 23, along with parameters for abstraction from the corresponding alkane. The kinetic data for methyl radical attack on trimethylsilane are in reasonable accord with those of Kerr, Slater and Young (99).
TABLE 22
Hydrogen Abstraction from Group IV Tetramethyls

<table>
<thead>
<tr>
<th>Species</th>
<th>E</th>
<th>Log A</th>
<th>Log k_{164}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃⁺ + Me₄C</td>
<td>10.0</td>
<td>11.3</td>
<td>6.3</td>
<td>105</td>
</tr>
<tr>
<td>CH₃⁺ + Me₄Si</td>
<td>10.3</td>
<td>11.5</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>11.6</td>
<td>6.4</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>12.6</td>
<td>7.1</td>
<td>104</td>
</tr>
<tr>
<td>CH₃⁺ + Me₄Ge</td>
<td>9.6</td>
<td>11.8</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>CH₃⁺ + Me₄Sn</td>
<td>8.6</td>
<td>11.1</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>CH₃⁺ + Me₄Pb</td>
<td>7.4</td>
<td>10.2</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>CF₃⁺ + Me₄C</td>
<td>7.6</td>
<td>11.8</td>
<td>8.0</td>
<td>60</td>
</tr>
<tr>
<td>CF₃⁺ + Me₄Si</td>
<td>7.6</td>
<td>12.0</td>
<td>8.2</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 23
Methyl Radicals          Trifluoromethyl Radicals

<table>
<thead>
<tr>
<th>Species</th>
<th>E</th>
<th>Log A</th>
<th>Log k_{164}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>6.9</td>
<td>11.8</td>
<td>8.3</td>
<td>p</td>
</tr>
<tr>
<td>Me₃SiH</td>
<td>7.8</td>
<td>11.3</td>
<td>7.4</td>
<td>p</td>
</tr>
<tr>
<td>Me₃CH</td>
<td>8.5</td>
<td>11.5</td>
<td>7.2</td>
<td>b</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>E</th>
<th>Log A</th>
<th>Log k_{164}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>14.5</td>
<td>11.8</td>
<td>4.5</td>
<td>a</td>
</tr>
<tr>
<td>Me₃SiH</td>
<td>7.8</td>
<td>11.3</td>
<td>7.4</td>
<td>p</td>
</tr>
<tr>
<td>Me₃CH</td>
<td>8.5</td>
<td>11.5</td>
<td>7.2</td>
<td>b</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>E</th>
<th>Log A</th>
<th>Log k_{164}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>14.5</td>
<td>11.8</td>
<td>4.5</td>
<td>a</td>
</tr>
<tr>
<td>Me₃SiH</td>
<td>7.8</td>
<td>11.3</td>
<td>7.4</td>
<td>p</td>
</tr>
<tr>
<td>Me₃CH</td>
<td>8.5</td>
<td>11.5</td>
<td>7.2</td>
<td>b</td>
</tr>
</tbody>
</table>

a: Mean of parameters from ref. 72.
b: From ref. 111, assuming zero-point energy difference of 1.2 kcal/mole.
c: From ref. 110, results assumed to be internally consistent, but brought into line with n-C₄H₁₀ results in chapter 3.
p: This work.

E is in kcal/mole, A and k_{164} in mole⁻¹·cm³·sec⁻¹.
For both silane and trimethylsilane the activation energy for abstraction by \( \text{CF}_3 \cdot \) is around 2 kcal/mole lower than that for \( \text{CH}_3 \cdot \). The activation energy for abstraction of hydrogen from methane is around 7 kcal/mole higher than that for silane, with both radicals, while there is little difference in the activation energy requirements for abstraction from \( \text{Me}_3\text{CH} \) and \( \text{Me}_3\text{SiH} \). With both radicals the activation energy requirement for abstraction from \( \text{H}_3\text{C}-\text{H} \) is 6.0 kcal/mole higher than that for \( \text{Me}_3\text{C}-\text{H} \), while the activation energy for abstraction from \( \text{H}_3\text{Si}-\text{H} \) is about 0.6 kcal/mole lower than that for \( \text{Me}_3\text{Si}-\text{H} \) for both radicals. In hydrocarbons the labile nature of tertiary hydrogen atoms may be interpreted in terms of bond polarisation leading to enhanced reactivity of the tertiary C-H bond. When silicon is substituted for carbon as the central atom, the situation is reversed, and the Si-H bond is stabilised by electron withdrawal.

Pauling Electronegativities

\[
\begin{align*}
\text{H} & : 2.1 \\
\text{C} & : 2.5 \\
\text{Si} & : 1.8
\end{align*}
\]

The Si-H bond strength in trimethylsilane is not known with any certainty, values reported for \( \text{D(Me}_3\text{Si-H}) \) ranging from 64 to 88 kcal/mole (105, 106, 107). The data recorded in Table 23 provide an excellent illustration of the effect of dipolar interactions in radical-molecule reactions.
For attack on the non-polar molecules CH₄ and SiH₄ by either radical, a value of 11.9 ± 1 is obtained for Log A. On a per-hydrogen atom basis this corresponds to 11.3, in excellent agreement with the observed A-factors for abstraction of the single tertiary hydrogen atom from the essentially non-polar isobutane molecule by either radical and from Me₃SiH by the essentially non-polar methyl radical. The A-factor for attack of the highly polar CF₃⁺ radical on the polar trimethylsilane molecule however, is 10 times greater.

\[ \text{Me}_3\text{Si} - \text{H} \quad \text{CF}_3^+ \]

This may be interpreted in terms of electrostatic attraction between the negatively charged hydrogen atom and the positively charged attacking radical. While the forces involved will be small by comparison with the total kinetic energy of the system, leaving the activation energy unaffected, the relatively long-range nature of such attractions may substantially increase the number of effective collisions, due to "harpooning," with consequent increase in the observed A-factor. If this interpretation is valid we should expect low A-factors for attack of CF₃⁺ radicals on hydrogen atoms bonded to atoms of high electronegativity.

\[ \text{MeO} - \text{H} \quad \text{CF}_3 \]

\[ \text{MeNH} - \text{H} \quad \text{CF}_3 \]

This is, in fact, found to be the case, as will be seen in later chapters.
CHAPTER 5

In view of the high electronegativity of oxygen, the abstraction of hydrogen from alcohols by polar radicals should involve considerable dipole-dipole interaction. To investigate this, trifluoromethyl radicals, generated by the photolysis of CF₃I, have been reacted with methanol and trideuteromethanol. The results obtained are given in Tables 24 to 26 and presented graphically in Figs. 15 to 18. When this work began, conflicting values had been reported for the Arrhenius parameters of the corresponding methyl radical reactions.

The hydrogen abstracted is underlined.

Recently (113) Gray has attributed this discrepancy to a heterogenous hydrogen exchange reaction between the hydroxyl group of the alcohol and the methyl groups of the radical source, acetone having been used by Shannon and Harrison, and hexadeuteroacetone by Shaw and Thynne. In order to overcome this difficulty Gray and Herod (114) have repeated the investigation using compatibly labelled methanol and acetone, i.e. CD₃COCD₃ with CD₃OD, and CH₃COCH₃ with CH₃OH and CD₃OH. The results are shown in Table 28, together with the corresponding parameters for abstraction by trifluoromethyl radicals.

### TABLE 27.

<table>
<thead>
<tr>
<th></th>
<th>Shannon and Harrison (117)</th>
<th>Shaw and Thynne (80)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
<td>Log A</td>
</tr>
<tr>
<td>CD₃OH</td>
<td>11·7</td>
<td>11·3</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>10·4</td>
<td>11·4</td>
</tr>
<tr>
<td>CD₃OH</td>
<td>6·4</td>
<td>9·3</td>
</tr>
</tbody>
</table>

The hydrogen abstracted is underlined.
### TABLE 24

Photolysis of TFMI in the Presence of Trideuteromethanol

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>CD₃OH</th>
<th>CF₃I</th>
<th>CF₃H</th>
<th>CF₃D</th>
<th>C₂F₆</th>
<th>RH</th>
<th>RD</th>
<th>1000/T</th>
<th>Log RH</th>
<th>Log RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>148</td>
<td>357.1</td>
<td>1200</td>
<td>0.395</td>
<td>1.59</td>
<td>1.72</td>
<td>0.077</td>
<td>0.877</td>
<td>4.64</td>
<td>2.10</td>
<td>2.80</td>
<td>0.666</td>
<td>1.322</td>
</tr>
<tr>
<td>155</td>
<td>357.1</td>
<td>1500</td>
<td>0.291</td>
<td>1.57</td>
<td>1.69</td>
<td>0.076</td>
<td>0.711</td>
<td>6.88</td>
<td>3.11</td>
<td>2.80</td>
<td>0.837</td>
<td>1.493</td>
</tr>
<tr>
<td>153</td>
<td>357.1</td>
<td>1800</td>
<td>0.249</td>
<td>1.76</td>
<td>1.62</td>
<td>0.073</td>
<td>0.650</td>
<td>8.08</td>
<td>3.66</td>
<td>2.80</td>
<td>0.907</td>
<td>1.563</td>
</tr>
<tr>
<td>152</td>
<td>370.2</td>
<td>1200</td>
<td>0.182</td>
<td>1.29</td>
<td>1.35</td>
<td>0.071</td>
<td>0.730</td>
<td>8.66</td>
<td>4.58</td>
<td>2.70</td>
<td>0.937</td>
<td>1.661</td>
</tr>
<tr>
<td>154</td>
<td>384.5</td>
<td>1800</td>
<td>0.278</td>
<td>1.50</td>
<td>1.72</td>
<td>0.109</td>
<td>0.617</td>
<td>7.88</td>
<td>4.97</td>
<td>2.60</td>
<td>0.897</td>
<td>1.697</td>
</tr>
<tr>
<td>147</td>
<td>384.6</td>
<td>2400</td>
<td>0.210</td>
<td>1.45</td>
<td>1.73</td>
<td>0.019</td>
<td>0.458</td>
<td>12.2</td>
<td>7.69</td>
<td>2.60</td>
<td>1.086</td>
<td>1.886</td>
</tr>
<tr>
<td>151</td>
<td>400.0</td>
<td>1800</td>
<td>0.202</td>
<td>1.43</td>
<td>1.67</td>
<td>0.125</td>
<td>0.638</td>
<td>10.3</td>
<td>7.72</td>
<td>2.50</td>
<td>1.014</td>
<td>1.887</td>
</tr>
<tr>
<td>149</td>
<td>400.0</td>
<td>2500</td>
<td>0.335</td>
<td>1.35</td>
<td>2.24</td>
<td>0.168</td>
<td>0.356</td>
<td>11.2</td>
<td>8.38</td>
<td>2.50</td>
<td>1.050</td>
<td>1.923</td>
</tr>
<tr>
<td>85</td>
<td>416.6</td>
<td>1800</td>
<td>0.348</td>
<td>0.788</td>
<td>2.25</td>
<td>0.199</td>
<td>0.357</td>
<td>10.8</td>
<td>9.59</td>
<td>2.40</td>
<td>1.034</td>
<td>1.982</td>
</tr>
<tr>
<td>150</td>
<td>416.8</td>
<td>1800</td>
<td>0.237</td>
<td>0.953</td>
<td>2.78</td>
<td>0.202</td>
<td>0.483</td>
<td>15.5</td>
<td>1.38</td>
<td>2.40</td>
<td>1.192</td>
<td>0.140</td>
</tr>
<tr>
<td>145</td>
<td>434.8</td>
<td>450</td>
<td>0.222</td>
<td>1.54</td>
<td>3.61</td>
<td>0.382</td>
<td>1.64</td>
<td>12.7</td>
<td>1.34</td>
<td>2.30</td>
<td>1.102</td>
<td>0.127</td>
</tr>
<tr>
<td>146</td>
<td>434.8</td>
<td>2000</td>
<td>0.213</td>
<td>1.47</td>
<td>2.45</td>
<td>0.259</td>
<td>0.471</td>
<td>16.7</td>
<td>1.77</td>
<td>2.30</td>
<td>1.224</td>
<td>0.214</td>
</tr>
</tbody>
</table>

CD₃OH and CF₃I are in 10⁻⁶ mole cm⁻³; CF₃H, CF₃D and C₂F₆ in 10⁻¹² mole cm⁻³ sec⁻¹

RH refers to abstraction from the OH group, RD to abstraction from CD₃.
### TABLE 25

Photolysis of TFMI in the Presence of Methanol

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>MeOH</th>
<th>TFMI</th>
<th>CF$_3$H</th>
<th>C$_2$H$_6$</th>
<th>R</th>
<th>1000/T</th>
<th>Log$_{10}$R</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>356.8</td>
<td>1200</td>
<td>0.496</td>
<td>1.38</td>
<td>3.69</td>
<td>7.34</td>
<td>8.7</td>
<td>2.80</td>
<td>0.940</td>
</tr>
<tr>
<td>45</td>
<td>357.0</td>
<td>1200</td>
<td>0.285</td>
<td>1.66</td>
<td>2.36</td>
<td>8.67</td>
<td>8.9</td>
<td>2.80</td>
<td>0.949</td>
</tr>
<tr>
<td>42</td>
<td>357.1</td>
<td>1800</td>
<td>0.369</td>
<td>1.49</td>
<td>2.49</td>
<td>5.55</td>
<td>9.0</td>
<td>2.80</td>
<td>0.954</td>
</tr>
<tr>
<td>38</td>
<td>370.2</td>
<td>1800</td>
<td>0.193</td>
<td>1.72</td>
<td>1.90</td>
<td>7.23</td>
<td>11.6</td>
<td>2.70</td>
<td>1.065</td>
</tr>
<tr>
<td>39</td>
<td>370.2</td>
<td>1800</td>
<td>0.570</td>
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<td>3.93</td>
<td>5.00</td>
<td>9.7</td>
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<td>0.987</td>
</tr>
<tr>
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<td>1200</td>
<td>0.363</td>
<td>1.47</td>
<td>3.72</td>
<td>6.89</td>
<td>12.3</td>
<td>2.60</td>
<td>1.090</td>
</tr>
<tr>
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<td>0.195</td>
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<td>2.77</td>
<td>9.20</td>
<td>14.8</td>
<td>2.60</td>
<td>1.170</td>
</tr>
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<td>600</td>
<td>0.593</td>
<td>1.23</td>
<td>7.29</td>
<td>7.34</td>
<td>14.3</td>
<td>2.50</td>
<td>1.155</td>
</tr>
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<td>6.51</td>
<td>5.20</td>
<td>14.6</td>
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<td>1.164</td>
</tr>
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<td>0.247</td>
<td>1.68</td>
<td>3.63</td>
<td>9.37</td>
<td>15.2</td>
<td>2.50</td>
<td>1.182</td>
</tr>
<tr>
<td>30</td>
<td>415.6</td>
<td>900</td>
<td>0.236</td>
<td>1.58</td>
<td>5.38</td>
<td>1.13</td>
<td>21.5</td>
<td>2.40</td>
<td>1.332</td>
</tr>
<tr>
<td>29</td>
<td>415.6</td>
<td>1800</td>
<td>0.240</td>
<td>1.60</td>
<td>4.67</td>
<td>7.92</td>
<td>21.9</td>
<td>2.40</td>
<td>1.340</td>
</tr>
<tr>
<td>20</td>
<td>416.2</td>
<td>200</td>
<td>0.230</td>
<td>0.99</td>
<td>6.95</td>
<td>3.51</td>
<td>16.1</td>
<td>2.40</td>
<td>1.207</td>
</tr>
<tr>
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<td>600</td>
<td>0.381</td>
<td>1.03</td>
<td>6.32</td>
<td>9.37</td>
<td>17.1</td>
<td>2.40</td>
<td>1.233</td>
</tr>
<tr>
<td>22</td>
<td>416.6</td>
<td>600</td>
<td>0.334</td>
<td>1.03</td>
<td>7.47</td>
<td>1.00</td>
<td>22.3</td>
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<td>1.348</td>
</tr>
<tr>
<td>23</td>
<td>416.6</td>
<td>600</td>
<td>0.340</td>
<td>1.04</td>
<td>7.20</td>
<td>0.826</td>
<td>23.3</td>
<td>2.40</td>
<td>1.367</td>
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<tr>
<td>31</td>
<td>434.1</td>
<td>240</td>
<td>0.386</td>
<td>1.07</td>
<td>11.7</td>
<td>1.81</td>
<td>22.7</td>
<td>2.30</td>
<td>1.356</td>
</tr>
<tr>
<td>32</td>
<td>435.0</td>
<td>600</td>
<td>0.397</td>
<td>1.10</td>
<td>9.31</td>
<td>0.848</td>
<td>25.1</td>
<td>2.30</td>
<td>1.400</td>
</tr>
<tr>
<td>33</td>
<td>435.0</td>
<td>600</td>
<td>0.229</td>
<td>1.56</td>
<td>6.01</td>
<td>1.09</td>
<td>25.1</td>
<td>2.30</td>
<td>1.400</td>
</tr>
</tbody>
</table>

MeOH and TFMI are in 10$^{-6}$ mole cm$^{-3}$; CF$_3$H and C$_2$F$_6$ in 10$^{-12}$ mole cm$^{-3}$ sec$^{-1}$. 
FIG. 15.

PHOTOLYSIS OF TPMI IN THE PRESENCE OF TRIDEUTEROMETHANOL

\[ \text{Log } R = \frac{1}{T} \cdot 2.7 \]

\[ \circ \text{CD}_3\text{OH} + \text{CF}_3^\cdot \rightarrow \text{CD}_3\text{O}^\cdot + \text{CF}_3\text{H} \]

\[ \circ \text{CD}_3\text{OH} + \text{CF}_3^\cdot \rightarrow \cdot\text{CD}_2\text{OH} + \text{CF}_3\text{D} \]
PHOTOLYSIS OF TFMI IN THE PRESENCE OF METHANOL

OVERALL ABSTRACTION OF HYDROGEN

FIG. 16.

Log R

1.5
1.0
0.5

2.3 2.4 2.5 2.6 2.7 2.8

1,000/T

TEST OF MECHANISM

FIG. 17.

$\frac{10^{-6}}{R_{CF_3}}$

10^{-6}[MeOH]/R_{CF_3}H
HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM CD₂OH

TABLE 26. - Relative Rates of Attack.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>161.6</th>
<th>143.4</th>
<th>126.8</th>
<th>111.4</th>
<th>97.2</th>
<th>83.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000/T</td>
<td>2.3</td>
<td>2.4</td>
<td>2.5</td>
<td>2.6</td>
<td>2.7</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>8.94</td>
<td>9.07</td>
<td>6.63</td>
<td>7.93</td>
<td>5.20</td>
<td>3.93</td>
</tr>
<tr>
<td>% CF₃D</td>
<td>10.61</td>
<td>9.38</td>
<td>6.43</td>
<td>6.02</td>
<td>5.47</td>
<td>4.37</td>
</tr>
<tr>
<td>(By mass-</td>
<td>9.29</td>
<td>7.73</td>
<td>6.87</td>
<td>4.27</td>
<td>5.63</td>
<td>5.14</td>
</tr>
<tr>
<td>spec.)</td>
<td>7.47</td>
<td>7.81</td>
<td>6.11</td>
<td>8.03</td>
<td>4.66</td>
<td>5.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.78</td>
<td>5.14</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.09</td>
<td>3.73</td>
</tr>
<tr>
<td>MEAN:</td>
<td>9.08</td>
<td>8.50</td>
<td>6.51</td>
<td>6.21</td>
<td>5.03</td>
<td>4.33</td>
</tr>
<tr>
<td>Log₁₀ MEAN</td>
<td>0.96</td>
<td>0.93</td>
<td>0.81</td>
<td>0.79</td>
<td>0.70</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The Temperature Dependence of the Relative Rates of Attack is shown in Fig. 18 below.

FIG.18
Methyl (114)     Trifluoromethyl (This work)  
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
   & \multicolumn{2}{|c|}{E} & \multicolumn{1}{|c|}{Log A} & \multicolumn{1}{|c|}{Log \textit{k}_{164}} & \multicolumn{2}{|c|}{E} & \multicolumn{1}{|c|}{Log A} & \multicolumn{1}{|c|}{Log \textit{k}_{164}} \\
\hline
CD\textsubscript{3}OH & 11.9 & 11.3 & 5.3 & 6.6 & 10.2 & 6.9 \\
CH\textsubscript{3}OH & 10.0 & 11.3 & 6.3 & 4.7 & 10.0 & 7.6 \\
CD\textsubscript{3}OH & 9.5 & 10.5 & 5.7 & 3.2 & 9.5 & 7.9 \\
\hline
\end{tabular}

\textbf{TABLE 28}

\textit{E} and \textit{A} in kcal/mole. \textit{k}_{164} in mole\textsuperscript{-1}cm\textsuperscript{3}sec\textsuperscript{-1}.

The hydrogen abstracted is underlined.

E is in kcal/mole. A and \textit{k}_{164} in mole\textsuperscript{-1}cm\textsuperscript{3}sec\textsuperscript{-1}.

With both radicals, the activation energy for abstraction from the hydroxyl group is lower than that for the methyl group, the difference being around 1 kcal/mole. At high temperatures, however, abstraction from the methyl position is favoured, the A-factor being about ten times greater.

Methanol is considerably more reactive with CF\textsubscript{3}· than with CH\textsubscript{3}·, by a factor of about 50 at 164°C, due to the marked lowering in activation energy requirements with the polar radical, the difference being around 6 kcal/mole for both positions. This is considerably in excess of the differences found for non-polar molecules, and may be compared with the low values obtained for silanes, where the polarity is reversed.

The activation energy for abstraction of hydrogen from the alkyl position by either radical is 1.9 kcal/mole lower than that for abstraction of deuterium. Since the zero-point energy difference corresponding to a single C-H and C-D stretching vibration is 1.2 kcal/mole the possibility of tunnelling cannot be ruled out.
As predicted in the previous chapter, the \( \text{A-factor} \) for abstraction from the hydroxyl group by \( \text{CF}_3^· \) is lower than that for \( \text{CH}_3^· \) (by a factor of ten), and is attributed to electrostatic repulsion between the molecule and the incoming radical. A similar lowering is observed for the methyl group. This is discussed more fully in Chapter 8, where Arrhenius parameters are compared for hydrogen abstraction from methyl groups in different chemical environments.

Results obtained by Carlton and his co-workers (70) for the abstraction of hydrogen from methanol by trifluoromethyl radicals differ markedly from those obtained in the present work. These investigators used hexafluorooazomethane as radical source. Due to rapid addition to theazo linkage the radical concentration obtained is low, and the \( \text{C}_2\text{F}_6 \) formed could not be measured accurately. Accordingly, a competitive technique was adopted, using

\[
\text{CF}_3^· + \text{CH}_4 \longrightarrow \text{CF}_3\text{H} + \text{CH}_3^·
\]
as reference reaction. The following parameters were obtained:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( E )</th>
<th>( \log A )</th>
<th>( \log k_{164} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CF}_3 + \text{CH}_3\text{OH} \longrightarrow \text{CF}_3\text{H} + \cdot\text{CH}_2\text{OH} )</td>
<td>8.3</td>
<td>12.2</td>
<td>8.0</td>
</tr>
<tr>
<td>( \longrightarrow \text{CF}_3\text{H} + \text{CH}_3^· )</td>
<td>8.3</td>
<td>11.2</td>
<td>7.0</td>
</tr>
</tbody>
</table>

\( E \) is in kcal/mole, \( A \) and \( k_{164} \) in \( \text{mole}^{-1}\text{cm}^3\text{sec}^{-1} \).

The overall rate constant for abstraction from \( \text{CH}_3\text{OH} \) at 164°C is in reasonable agreement with that obtained in the present work. Observed relative rates of attack on
CD$_3$OH, however, differ radically. For example, at 380°C Carlton reports a ratio of 1.08, as opposed to 0.060. (Fig. 18).

It is suggested that this may be due to disproportionation of the trideuteromethoxy radical with CF$_3^\cdot$.

\[
\begin{align*}
\text{CF}_3^\cdot + \text{CD}_3\text{OH} & \rightarrow \text{CF}_3\text{H} + \text{CD}_3\text{O}^\cdot \\
\text{CF}_3\text{D} + \cdot\text{CD}_2\text{OH} & \rightarrow \text{D}^\cdot\text{COD} + \text{CF}_3\text{D} \\
\text{COD}^\cdot + \text{CF}_3\text{D} & \rightarrow \text{CF}_3^\cdot \\
\text{CO} + \text{CF}_3\text{D} & 
\end{align*}
\]

As detailed in Chapter 3, when CF$_3$I is used as radical source, the presence in the system of high concentrations of iodine atoms, in equilibrium with molecular iodine, appears to inhibit secondary reactions.

In the course of this work an attempt was also made to investigate the kinetics of hydrogen atom abstraction from methyl mercaptan by trifluoromethyl radicals, the corresponding methyl radical reactions having been studied previously by Greig and Thynne (115) whose results are recorded below:

\[
\begin{align*}
\text{CH}_3^\cdot + \text{CD}_3\text{SH} & \rightarrow \text{CH}_4 + \text{CD}_3\text{S}^\cdot \\
\text{CH}_3\text{D} + \text{CD}_2\text{SH} & 
\end{align*}
\]

\[
\begin{align*}
E & \quad \log A & \quad \log k_{164} \\
4.1 & \quad 11.0 & \quad 8.9 \\
8.3 & \quad 10.9 & \quad 6.7
\end{align*}
\]

E is in kcal/mole, A and $k_{164}$ in mole$^{-1}$cm$^3$sec$^{-1}$. 
It was evident from preliminary runs, however, that the rate of abstraction by CF$_3^*$ was so great that the yield of C$_2$F$_6$ could not be measured with any degree of accuracy. By comparison of the relative rates of formation of CF$_3$H and C$_2$F$_6$ with those for runs performed under similar conditions using trimethylamine, the most labile hydrogen substrate fully investigated (Chapter 6), an estimate of $R$ at 40°C was obtained. For trimethylamine, $R_{40} = 110$; the value for methyl mercaptan is about twenty times greater, thus

$$R_{40}(\text{CH}_3\text{SH}) \approx 2000 \quad \therefore \quad \log R \approx 3.2$$

$$\therefore \quad \log k \approx 10.0 \text{ at } 40^\circ C.$$ 

Preliminary investigation of the photolysis of HFA in the presence of dimethylsulphide suggests that in the case of abstraction from CH$_3$SH less than 1% of the fluoroform results from abstraction from the methyl group. This is in accord with the work of Greig and Thynne for methyl radical attack on CD$_3$SH.

Since the Pauling electronegativity for sulphur is the same as that for carbon, we would not expect to find the $A$-factor depression observed for methanol. Taking the value of $\log A = 11.3$ found for abstraction from a non-polar site (Chapter 4) in conjunction with the estimated value of $\log k_{40} = 10$, gives an activation energy of about 2 kcal/mole for abstraction from the thiol group by CF$_3^*$. In Table 29 these estimated Arrhenius parameters are compared with parameters reported for related abstractions.
<table>
<thead>
<tr>
<th></th>
<th>METHYL RADICALS</th>
<th></th>
<th>TRIFLUOROMETHYL RADICALS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
<td>Log A</td>
<td>Log ( k_{164} )</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>3.1</td>
<td>11.8</td>
<td>10.2</td>
</tr>
<tr>
<td>( \text{CD}_3\text{SH} )</td>
<td>4.1</td>
<td>11.0</td>
<td>8.9</td>
</tr>
<tr>
<td>( \text{CH}_3\text{OH} )</td>
<td>9.5</td>
<td>10.5</td>
<td>5.7</td>
</tr>
</tbody>
</table>

\( E \) is in kcal/mole, \( A \) and \( k_{164} \) in mole\(^{-1}\)cm\(^3\)sec\(^{-1}\).

The hydrogen atom abstracted is underlined.

Three sets of Arrhenius parameters have been reported for the reaction:

\[
\text{CF}_3 + \text{H}_2\text{S} \rightarrow \text{CF}_3\text{H} + \text{SH}
\]

Two of these were obtained by N.L. Arthur working in different Laboratories (69, 116), the third by Kale and Timmons (71) who report an extremely low activation energy, but normal A-factor. The difference between these determinations results from a ten-fold discrepancy in observed rate constants, and cannot be explained in terms of compensation of Arrhenius parameters. The high reactivity of methyl mercaptan towards \( \text{CF}_3^- \) attack appears to lend support to the higher values reported by Kale and Timmons. On the basis of their work, and the parameters estimated for \( \text{CH}_3\text{SH} \), the activation energy requirement for hydrogen atom abstraction from S-H by \( \text{CH}_3^- \) is around 2 kcal/mole greater than for \( \text{CF}_3^- \).

Greig and Thynne have reported Arrhenius parameters for the reaction

\[
\text{CH}_3^- + \text{CD}_3\text{SH} \rightarrow \text{CH}_3\text{SH} + \text{CD}_3^-
\]
A similar group abstraction was observed for trifluoromethyl radical attack on methanol.

\[
\text{CF}_3^\cdot + \text{CD}_3\text{OH} \rightarrow \text{CF}_3\text{OH} + \text{CD}_3^\cdot
\]

When CF\textsubscript{3}I was photolysed in the presence of CD\textsubscript{3}OH, small amounts of products volatile at -196°C were formed. Mass-spectrometric analysis showed these to be CD\textsubscript{3}H and CD\textsubscript{4} formed by the following reactions.

\[
\text{CD}_3^\cdot + \text{CD}_3\text{OH} \rightarrow \text{CD}_4 + \cdot\text{CD}_2\text{OH}
\]

\[
\rightarrow \text{CD}_3\text{H} + \text{CD}_3\cdot
\]
CHAPTER 6

When this work was started, in 1966, no kinetic data had been reported for hydrogen abstraction reactions involving the severing of an N-H bond by CF$_3^\cdot$. Accordingly a study was made of the photolysis of CF$_3$I in the presence of ammonia, all fluoroform and hexafluoroethane being attributed to the following reactions.

\[
\begin{align*}
\text{CF}_3\text{I} + \text{hv} & \rightarrow \text{CF}_3^\cdot + \text{I}^\cdot \\
\text{CF}_3^\cdot + \text{CF}_3^\cdot & \rightarrow \text{C}_2\text{F}_6 \\
\text{CF}_3^\cdot + \text{NH}_3 & \rightarrow \text{CF}_3\text{H} + \text{NH}_2^\cdot
\end{align*}
\]

**TABLE 30**

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>NH$_3$</th>
<th>CF$_3$I</th>
<th>CF$_3$H</th>
<th>C$_2$F$_6$</th>
<th>R</th>
<th>1000/T</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>229</td>
<td>303.0</td>
<td>450</td>
<td>1.99</td>
<td>1.95</td>
<td>0.90</td>
<td>4.97</td>
<td>0.204</td>
<td>3.30</td>
<td>1.31</td>
</tr>
<tr>
<td>232</td>
<td>322.6</td>
<td>450</td>
<td>2.08</td>
<td>2.04</td>
<td>1.12</td>
<td>4.77</td>
<td>0.247</td>
<td>3.10</td>
<td>1.39</td>
</tr>
<tr>
<td>227</td>
<td>344.8</td>
<td>450</td>
<td>4.86</td>
<td>0.99</td>
<td>3.58</td>
<td>4.31</td>
<td>0.355</td>
<td>2.90</td>
<td>1.55</td>
</tr>
<tr>
<td>230</td>
<td>370.3</td>
<td>450</td>
<td>1.76</td>
<td>1.72</td>
<td>1.89</td>
<td>3.50</td>
<td>0.577</td>
<td>2.70</td>
<td>1.76</td>
</tr>
<tr>
<td>248</td>
<td>384.6</td>
<td>450</td>
<td>2.74</td>
<td>1.50</td>
<td>2.64</td>
<td>1.69</td>
<td>0.741</td>
<td>2.60</td>
<td>1.87</td>
</tr>
<tr>
<td>231</td>
<td>400.0</td>
<td>450</td>
<td>1.53</td>
<td>1.50</td>
<td>3.13</td>
<td>3.56</td>
<td>1.08</td>
<td>2.50</td>
<td>0.03</td>
</tr>
<tr>
<td>247</td>
<td>416.6</td>
<td>500</td>
<td>2.56</td>
<td>1.41</td>
<td>4.12</td>
<td>1.13</td>
<td>1.52</td>
<td>2.40</td>
<td>0.18</td>
</tr>
<tr>
<td>226</td>
<td>434.8</td>
<td>450</td>
<td>5.85</td>
<td>1.19</td>
<td>22.5</td>
<td>3.25</td>
<td>2.13</td>
<td>2.30</td>
<td>0.33</td>
</tr>
<tr>
<td>246</td>
<td>454.5</td>
<td>450</td>
<td>2.53</td>
<td>1.39</td>
<td>6.21</td>
<td>0.63</td>
<td>3.10</td>
<td>2.20</td>
<td>0.49</td>
</tr>
<tr>
<td>245</td>
<td>500.0</td>
<td>500</td>
<td>2.38</td>
<td>1.31</td>
<td>12.4</td>
<td>0.25</td>
<td>10.4</td>
<td>2.00</td>
<td>1.02</td>
</tr>
<tr>
<td>244</td>
<td>555.5</td>
<td>300</td>
<td>2.62</td>
<td>1.44</td>
<td>62.5</td>
<td>0.24</td>
<td>48.4</td>
<td>1.80</td>
<td>1.68</td>
</tr>
<tr>
<td>243</td>
<td>625.2</td>
<td>450</td>
<td>1.78</td>
<td>0.98</td>
<td>4.80</td>
<td>0.34</td>
<td>461</td>
<td>1.60</td>
<td>2.66</td>
</tr>
</tbody>
</table>

NH$_3$ and CF$_3$I are in $10^{-6}$ moles cm$^{-3}$; CF$_3$H and C$_2$F$_6$ in $10^{-12}$ mole cm$^{-3}$ sec$^{-1}$. 
FIG. 19.  
$\text{CF}_3^- + \text{AMMONIA}$

FIG. 20.  TEST OF MECHANISM (60°C)

$\frac{10^{-6}}{R_{\text{CF}_3\text{H}}^{\text{2}_2\text{F}_6}}$

$\theta$ METHYLAMINE
$\circ$ AMMONIA $10^{-6}[\text{RH}] / R_{\text{CF}_3\text{H}}$
The resulting Arrhenius plot for $k_a$, however, showed marked curvature (Table 30 and Fig. 19). Since it is evident that the rate of abstraction from ammonia is considerably lower than that for other substrates studied, contamination was immediately suspected. Accordingly a new vacuum system was constructed (a simplified version of the line described in Chapter 2) avoiding the use of hydrocarbon grease. Two different samples of ammonia were used: ICI redistilled ammonia was bulb-to-bulb distilled, a middle fraction being stored at -196°C; a sample prepared by heating an intimate mixture of soda-lime and ammonium chloride was purified by repeated slush-bath distillation: preliminary runs showed the samples to react with $\text{CF}_3^\cdot$ at identical rates. No systematic variation of $R$ with run time, which would be expected if traces of a highly reactive impurity were being used up preferentially, was observed.

The reaction was then studied at four different temperatures, using a wide range of run times and reactant concentrations: the results are recorded in Table 31. In Fig. 20 $1/R_{\text{DF}_{6}}^{\frac{1}{3}}$ at 60°C is plotted against $[\text{NH}]/R_{\text{DF}_{3}^H}$. A similar plot is shown for $\text{CH}_3\text{NH}_2$ (Table 32). It is evident that while for methylamine $R$ is independent of radical concentration, the same is not true for ammonia. Figs. 21 and 22 show similar plots at each of the temperatures studied: while the graphs appear to be linear they do not pass through the origin.
### TABLE 31

**CF₃⁻ Attack on Ammonia: Clean Vacuum System.**

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>NH₃</th>
<th>CF₃I</th>
<th>CF₃H</th>
<th>C₂F₆</th>
<th>1000 T</th>
<th>NH₃/CF₃H</th>
<th>1/C₂F₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>348</td>
<td>333.3</td>
<td>3600</td>
<td>1.21</td>
<td>1.21</td>
<td>0.296</td>
<td>0.687</td>
<td>3.00</td>
<td>4.10</td>
<td>1.21</td>
</tr>
<tr>
<td>346</td>
<td>333.3</td>
<td>1800</td>
<td>1.11</td>
<td>0.29</td>
<td>0.237</td>
<td>0.762</td>
<td>3.00</td>
<td>4.70</td>
<td>1.15</td>
</tr>
<tr>
<td>352</td>
<td>333.3</td>
<td>3600</td>
<td>4.11</td>
<td>0.42</td>
<td>0.217</td>
<td>0.642</td>
<td>3.00</td>
<td>18.9</td>
<td>1.25</td>
</tr>
<tr>
<td>366</td>
<td>333.3</td>
<td>3600</td>
<td>2.94</td>
<td>0.70</td>
<td>0.133</td>
<td>0.534</td>
<td>3.00</td>
<td>22.1</td>
<td>1.37</td>
</tr>
<tr>
<td>361</td>
<td>370.4</td>
<td>3600</td>
<td>0.91</td>
<td>1.96</td>
<td>0.669</td>
<td>0.700</td>
<td>2.70</td>
<td>1.36</td>
<td>1.20</td>
</tr>
<tr>
<td>360</td>
<td>370.4</td>
<td>3600</td>
<td>1.30</td>
<td>1.33</td>
<td>0.546</td>
<td>0.590</td>
<td>2.70</td>
<td>2.37</td>
<td>1.30</td>
</tr>
<tr>
<td>367</td>
<td>370.4</td>
<td>3600</td>
<td>2.45</td>
<td>0.59</td>
<td>0.161</td>
<td>0.228</td>
<td>2.70</td>
<td>15.2</td>
<td>2.10</td>
</tr>
<tr>
<td>344</td>
<td>434.8</td>
<td>1800</td>
<td>1.40</td>
<td>0.37</td>
<td>0.995</td>
<td>0.742</td>
<td>2.30</td>
<td>1.41</td>
<td>1.16</td>
</tr>
<tr>
<td>345</td>
<td>434.8</td>
<td>1800</td>
<td>1.35</td>
<td>0.35</td>
<td>0.914</td>
<td>0.625</td>
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<td>1800</td>
<td>2.28</td>
<td>0.23</td>
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<td>2.19</td>
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<td>1800</td>
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<td>0.406</td>
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<td>3.55</td>
<td>1.78</td>
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<td>434.8</td>
<td>7200</td>
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<td>0.228</td>
<td>2.30</td>
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<td>2.10</td>
</tr>
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<td>1.11</td>
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<td>0.273</td>
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<td>1.02</td>
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<td>12000</td>
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<td>1.036</td>
<td>0.165</td>
<td>2.00</td>
<td>1.38</td>
<td>2.47</td>
</tr>
</tbody>
</table>

NH₃ and CF₃I are in 10⁻⁶ mole cm⁻³;
CF₃H and C₂F₆ in 10⁻¹² mole cm⁻³sec⁻¹;
NH₃/CF₃H in 10⁶ sec., and 1/(C₂F₆)³ in
10⁶ mole⁻³ cm² sec⁻³.
PHOTOLYSIS OF TFMT IN THE PRESENCE OF AMMONIA

FIG. 21.

\[ \frac{10^{-6}}{R_{C_2F_6}} \]

\[ 10^{-6}[\text{NH}_3]/R_{CF_3H} \]

1000/T = 2.7

1000/T = 3.0

FIG. 22.

\[ \frac{10^{-6}}{R_{C_2F_6}} \]

\[ 10^{-6}[\text{NH}_3]/R_{CF_3H} \]

1000/T = 2.0

1000/T = 2.3
While no conclusive explanation of these observations may be advanced, it seems probable that reactions of \( \text{NH}_2^\cdot \) radicals formed by the primary abstraction process will complicate the mechanism. If we suppose these radicals to give rise to some intermediate \( \text{XH} \), then additional fluoroform will result from the reaction:

\[
\text{XH} + \text{CF}_3 \rightarrow \text{CF}_3\text{H} + \cdot \text{(k}_x\text{)}
\]

Thus

\[
R_{\text{CF}_3\text{H}} = k_a[\text{CF}_3][\text{NH}_3] + k_x[\text{CF}_3][\text{XH}] = \frac{1}{k_c} \left[ \frac{R_{\text{CF}_3\text{H}}}{R_2^\frac{2}{F_6}} \right] \left[ k_a[\text{NH}_3] + k_x[\text{XH}] \right]
\]

If \( \text{XH} \) arises from \( \text{NH}_2^\cdot \), it seems reasonable to suppose that

\[
[XH] \ll R_{\text{NH}_2} \quad \text{i.e.} \quad [XH] = c R_{\text{CF}_3\text{H}}
\]

where \( c \) is a (temperature dependent) constant.

\[
R_{\text{CF}_3\text{H}} = \frac{1}{k_c} \left[ k_a[\text{NH}_3] + c k_x R_{\text{CF}_3\text{H}} \right]
\]

\[
\frac{1}{R_{\text{CF}_3\text{H}}} = \frac{k_a}{k_c} [\text{NH}_3] + c k_x
\]

Thus the gradient of a plot of \( 1/R_{\text{CF}_3\text{H}} \) against \( [\text{NH}_3]/R_{\text{CF}_3\text{H}} \) should equal \( k_a/k_c \), as in previous systems.

Plotting Log GRADIENT against \( 1,000/T \) for the graphs shown in Figs. 21 and 22 gives a linear plot corresponding to the following Arrhenius parameters. (Fig. 23)

\[
E = 9 \pm 1 \text{ kcal/mole} \quad \text{Log } A = 10.8 \pm 0.4 \text{ (mole}^{-1}\text{cm}^3\text{sec}^{-1})
\]
This Arrhenius Plot uses the gradients of the plots in Figs. 21 and 22 on P. 112.
In view of the speculative nature of the above treatment it would be unwise to attach any great significance to these parameters. It is evident, however, that the mechanism is considerably more complex than was at first expected. Results reported subsequently by Gray, Arthur and Lloyd (119), using the same radical source, and attributing CF₃H formation solely to the initial abstraction reaction are also indicated in Fig. 19. Over the somewhat narrower temperature range used, the gradient of the Arrhenius plot based on their results corresponds closely to that of the preliminary plot obtained in the present investigation. Unfortunately, the conditions used by these workers did not vary sufficiently to allow the test of mechanism described above to be applied to their data.

Whatever the nature of the complications in the ammonia system, it is clear from Fig. 20 that they do not occur in the case of methylamine, which was also studied in the course of this work. CF₃I was photolysed in the presence of CH₃NH₂, and with CD₃NH₂; the results are recorded in tables 32 and 33 and presented graphically in Figs. 24 and 25. The Arrhenius parameters derived are listed in Table 34 together with those reported by Gray and Thynne (81) for the corresponding reactions of methyl radicals.

The parameters for the NH₂ group are the first to be reported for a reaction in which a hydrogen atom bonded to nitrogen is abstracted by a trifluoromethyl radical.
TABLE 32

Photolysis of TFMI in the Presence of Methylamine.

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>MeNH₂</th>
<th>CF₃I</th>
<th>CF₃H</th>
<th>C₂F₆</th>
<th>R</th>
<th>(\frac{1000}{T})</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>177</td>
<td>302·9</td>
<td>100</td>
<td>1·21</td>
<td>1·22</td>
<td>90·1</td>
<td>57·7</td>
<td>9·82</td>
<td>3·30</td>
<td>0·994</td>
</tr>
<tr>
<td>169</td>
<td>303·1</td>
<td>200</td>
<td>1·25</td>
<td>1·86</td>
<td>48·9</td>
<td>69·3</td>
<td>9·40</td>
<td>3·30</td>
<td>0·977</td>
</tr>
<tr>
<td>170</td>
<td>312·4</td>
<td>50</td>
<td>1·51</td>
<td>1·54</td>
<td>78·3</td>
<td>70·7</td>
<td>18·0</td>
<td>3·20</td>
<td>1·257</td>
</tr>
<tr>
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<td>322·6</td>
<td>100</td>
<td>1·12</td>
<td>1·13</td>
<td>12·8</td>
<td>48·9</td>
<td>16·3</td>
<td>3·10</td>
<td>1·215</td>
</tr>
<tr>
<td>318</td>
<td>333·3</td>
<td>50</td>
<td>0·903</td>
<td>0·97</td>
<td>50·0</td>
<td>4·64</td>
<td>25·7</td>
<td>3·00</td>
<td>1·411</td>
</tr>
<tr>
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<td>333·3</td>
<td>50</td>
<td>0·657</td>
<td>1·95</td>
<td>11·5</td>
<td>66·8</td>
<td>21·5</td>
<td>3·00</td>
<td>1·333</td>
</tr>
<tr>
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<td>333·3</td>
<td>50</td>
<td>0·193</td>
<td>1·97</td>
<td>40·4</td>
<td>45·5</td>
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<td>1·498</td>
</tr>
<tr>
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<td>333·3</td>
<td>500</td>
<td>1·59</td>
<td>1·95</td>
<td>8·47</td>
<td>3·37</td>
<td>29·3</td>
<td>3·00</td>
<td>1·467</td>
</tr>
<tr>
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<td>0·892</td>
<td>33·8</td>
<td>1·86</td>
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<td>1·394</td>
</tr>
<tr>
<td>323</td>
<td>333·3</td>
<td>600</td>
<td>1·48</td>
<td>0·559</td>
<td>32·1</td>
<td>0·637</td>
<td>27·3</td>
<td>3·00</td>
<td>1·435</td>
</tr>
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<td>179</td>
<td>344·6</td>
<td>150</td>
<td>0·84</td>
<td>0·849</td>
<td>11·2</td>
<td>26·8</td>
<td>25·5</td>
<td>2·90</td>
<td>1·411</td>
</tr>
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<td>18·0</td>
<td>33·5</td>
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<td>57·4</td>
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<td>1·761</td>
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<td>100</td>
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<td>0·938</td>
<td>18·5</td>
<td>8·68</td>
<td>67·2</td>
<td>2·50</td>
<td>1·832</td>
</tr>
<tr>
<td>165</td>
<td>416·3</td>
<td>180</td>
<td>0·388</td>
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<td>79·7</td>
<td>9·66</td>
<td>66·1</td>
<td>2·40</td>
<td>1·830</td>
</tr>
<tr>
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<td>416·3</td>
<td>100</td>
<td>0·348</td>
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<td>93·0</td>
<td>13·1</td>
<td>73·7</td>
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<td>9·08</td>
<td>109</td>
<td>2·30</td>
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</table>

MeNH₂ and CF₃I are in \(10^-6\) moles cm\(^{-3}\);
CF₃H and C₂F₆ are in \(10^-12\) mole cm\(^{-3}\)sec\(^{-1}\).
TABLE 33

Photolysis of TFMI in the Presence of Trideuteromethylamine

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>CD₃NH₂</th>
<th>CF₃I</th>
<th>CF₃H</th>
<th>CF₃D</th>
<th>C₂F₆</th>
<th>R_H</th>
<th>R_D</th>
<th>1000 T</th>
<th>Log R_H</th>
<th>Log R_D</th>
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<td>183</td>
<td>302.9</td>
<td>250</td>
<td>1.15</td>
<td>1.74</td>
<td>9.82</td>
<td>5.53</td>
<td>29.2</td>
<td>1.59</td>
<td>0.89</td>
<td>3.30</td>
<td>0.200</td>
<td>1.950</td>
</tr>
<tr>
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<td>303.2</td>
<td>150</td>
<td>1.19</td>
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<td>6.49</td>
<td>24.0</td>
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<td>1.10</td>
<td>3.30</td>
<td>0.209</td>
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<td>0.68</td>
<td>4.39</td>
<td>3.84</td>
<td>20.5</td>
<td>1.59</td>
<td>1.40</td>
<td>3.20</td>
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</tr>
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<td>7.13</td>
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<td>3.00</td>
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<tr>
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<td>1.00</td>
<td>10.3</td>
<td>10.8</td>
<td>20.9</td>
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<tr>
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<td>6.77</td>
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<td>0.591</td>
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<td>8.86</td>
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<td>5.81</td>
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<td>500</td>
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<td>0.59</td>
<td>7.86</td>
<td>13.0</td>
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<td>6.85</td>
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<td>0.836</td>
<td>1.053</td>
</tr>
<tr>
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<td>0.96</td>
<td>1.01</td>
<td>19.2</td>
<td>25.9</td>
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<td>15.8</td>
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</tr>
<tr>
<td>191</td>
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<td>450</td>
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<td>0.60</td>
<td>14.9</td>
<td>22.5</td>
<td>3.71</td>
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<td>21.9</td>
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<td>0.82</td>
<td>14.1</td>
<td>23.5</td>
<td>2.95</td>
<td>13.7</td>
<td>22.7</td>
<td>2.30</td>
<td>1.137</td>
<td>1.357</td>
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</table>

CD₃NH₂ and CF₃I are in 10⁻⁶ mole cm⁻³; CF₃H, CF₃D and C₂F₆ are in 10⁻¹² mole cm⁻³ sec⁻¹.
HYDROGEN ABSTRACTION FROM AMINES BY CF₃⁺

**FIG. 24.**

Log R

<table>
<thead>
<tr>
<th>1,000/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
</tr>
<tr>
<td>2.5</td>
</tr>
<tr>
<td>2.7</td>
</tr>
<tr>
<td>2.9</td>
</tr>
<tr>
<td>3.1</td>
</tr>
<tr>
<td>3.3</td>
</tr>
</tbody>
</table>

Overall Abstraction from (CH₃)₂NH by CF₃⁺

- " " " CH₃NH₂ " "

△ CF₃⁺ + CD₃NH₂ → CF₃H + CD₃NH⁺
FIG. 25. \[ \text{CD}_2\text{NH}_2 + \text{CF}_3 \cdot \longrightarrow \cdot \text{CD}_2\text{NH}_2 + \text{CF}_3\text{D} \]

\[ \log R \]

\[ \frac{1}{1,000/T} \]

FIG. 26.

\[ \log R \]

\[ \frac{1}{1,000/T} \]

- \( (\text{CH}_3)_2\text{ND} + \text{CF}_3 \cdot \longrightarrow (\text{CH}_3)_2\text{NDCH}_2 \cdot + \text{CF}_3\text{H} \)
- \( (\text{CH}_3)_2\text{ND} + \text{CF}_3 \cdot \longrightarrow (\text{CH}_3)_2\text{N} \cdot + \text{CF}_3\text{D} \)
The atom abstracted is underlined.

The kinetic isotope effect of 1.9 kcal/mole exceeds considerably the zero-point energy difference of 1.2 kcal/mole for a single C-H and C-D stretching vibration. This is in accord with the results reported in the previous chapter for abstraction from CH$_3$OH and CD$_3$OH by both CF$_3$· and CH$_3$·, and once more may indicate tunnelling.

As predicted in Chapter 4, depression of the A-factor is observed from the reaction:

\[
\text{CH}_3\text{NH}_2 + \text{CF}_3\cdot \rightarrow \text{CH}_3\text{NH}^+ + \text{CF}_3\text{H}
\]

due to dipolar repulsion between the molecule and the attacking radical. The effect is less pronounced than in the case of methanol, as would be expected from the Pauling electronegativities of oxygen and nitrogen (3.5 and 3.0 respectively). As will be seen from Table 34, Gray and Thynne report a low A-Factor for the corresponding methyl radical reaction. The overall activation energy

<table>
<thead>
<tr>
<th>Methyl Radicals</th>
<th>E</th>
<th>Log A</th>
<th>Log $k_{164}$</th>
<th>Trifluoromethyl Radicals</th>
<th>AE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NH$_2$</td>
<td>7.2</td>
<td>10.6</td>
<td>7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(overall)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.0</td>
</tr>
</tbody>
</table>

E is in kcal/mole, A and $k_{164}$ in mole$^{-1}$cm$^3$sec$^{-1}$
for hydrogen abstraction from \( \text{CH}_3\text{NH}_2 \) by methyl radicals exceeds that for \( \text{CF}_3^- \) by 3.0 kcal/mole, in excellent agreement with the value established by Pritchard. For abstraction from the methyl group, however, the difference is 4.5 kcal/mole, while for the amino group it is only 1.6 kcal/mole, this low value being coupled with the low A-factor mentioned above. Severe analytical difficulties were encountered in the methyl radical work due to abstraction from the radical source, azomethane. (109)

\[
\text{CH}_3^- + \text{CH}_3\text{N}_2\text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_3\text{N}_2\text{CH}_2^-.
\]

For an equimolar mixture of azomethane and \( \text{CD}_3\text{NH}_2 \), the methane produced on photolysis at \( 164^\circ \text{C} \) would be made up as follows:

- \( \text{CH}_4 \) from AZOMETHANE - 60%
- \( \text{CH}_4 \) from \( \text{CD}_3\text{NH}_2 \) - 36%
- \( \text{CH}_3\text{D} \) from \( \text{CD}_3\text{NH}_2 \) - 4%

Thus, as well as the error involved in analysing for such a small percentage of \( \text{CH}_3\text{D} \), calculation of methane formed by abstraction from the amino group would involve relatively small differences between large quantities, with consequent accumulation of error. In particular a small error in the Arrhenius parameters for the above abstraction from the radical source would produce a considerably larger error in the parameters for the reaction

\[
\text{CH}_3^- + \text{CD}_3\text{NH}_2 \rightarrow \text{CH}_4 + \text{CD}_3\text{NH}^-.
\]

It seems likely, therefore, that the low A-factor reported for this reaction may be incorrect, particularly in view of the normal A-factor reported for abstraction of hydrogen from the hydroxyl group in methanol by \( \text{CH}_3^- \). (114)
### TABLE 35

Photolysis of TFMI in the Presence of Dimethylamine

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>Me₂NH</th>
<th>CF₃I</th>
<th>CF₃H</th>
<th>C₂F₆</th>
<th>R</th>
<th>( \frac{1000}{T} )</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>370.3</td>
<td>90</td>
<td>.295</td>
<td>.767</td>
<td>228.</td>
<td>14.5</td>
<td>211</td>
<td>2.70</td>
<td>2.324</td>
</tr>
<tr>
<td>276</td>
<td>370.3</td>
<td>45</td>
<td>.554</td>
<td>.794</td>
<td>357</td>
<td>8.53</td>
<td>224</td>
<td>2.70</td>
<td>2.350</td>
</tr>
<tr>
<td>327</td>
<td>357.1</td>
<td>90</td>
<td>.694</td>
<td>.690</td>
<td>44.1</td>
<td>0.14</td>
<td>170</td>
<td>2.80</td>
<td>2.231</td>
</tr>
<tr>
<td>328</td>
<td>344.8</td>
<td>300</td>
<td>.183</td>
<td>1.83</td>
<td>25.8</td>
<td>0.84</td>
<td>156</td>
<td>2.90</td>
<td>2.194</td>
</tr>
<tr>
<td>330</td>
<td>344.8</td>
<td>900</td>
<td>.187</td>
<td>1.87</td>
<td>28.6</td>
<td>1.28</td>
<td>145</td>
<td>2.90</td>
<td>2.162</td>
</tr>
<tr>
<td>253</td>
<td>333.3</td>
<td>150</td>
<td>1.25</td>
<td>1.26</td>
<td>193</td>
<td>2.12</td>
<td>107</td>
<td>3.00</td>
<td>2.031</td>
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<td>45</td>
<td>.481</td>
<td>1.25</td>
<td>328</td>
<td>40.6</td>
<td>108</td>
<td>3.00</td>
<td>2.035</td>
</tr>
<tr>
<td>275</td>
<td>333.3</td>
<td>45</td>
<td>.902</td>
<td>1.29</td>
<td>490</td>
<td>27.1</td>
<td>106</td>
<td>3.00</td>
<td>2.023</td>
</tr>
<tr>
<td>331</td>
<td>322.6</td>
<td>1100</td>
<td>.124</td>
<td>1.24</td>
<td>11.5</td>
<td>1.02</td>
<td>96.5</td>
<td>3.10</td>
<td>1.984</td>
</tr>
<tr>
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<td>322.6</td>
<td>90</td>
<td>.479</td>
<td>1.36</td>
<td>30.3</td>
<td>0.52</td>
<td>88.6</td>
<td>3.10</td>
<td>1.947</td>
</tr>
<tr>
<td>333</td>
<td>322.6</td>
<td>900</td>
<td>.476</td>
<td>1.35</td>
<td>31.7</td>
<td>0.45</td>
<td>102</td>
<td>3.10</td>
<td>2.009</td>
</tr>
<tr>
<td>271</td>
<td>312.7</td>
<td>90</td>
<td>.591</td>
<td>1.54</td>
<td>307</td>
<td>54.2</td>
<td>72.2</td>
<td>3.20</td>
<td>1.858</td>
</tr>
<tr>
<td>336</td>
<td>303.0</td>
<td>300</td>
<td>.345</td>
<td>1.66</td>
<td>18.8</td>
<td>0.75</td>
<td>63.5</td>
<td>3.30</td>
<td>1.803</td>
</tr>
<tr>
<td>337</td>
<td>303.0</td>
<td>1500</td>
<td>.359</td>
<td>1.73</td>
<td>13.8</td>
<td>0.39</td>
<td>63.5</td>
<td>3.30</td>
<td>1.802</td>
</tr>
</tbody>
</table>

Me₂NH and CF₃I are in 10⁻⁶ mole cm⁻³
CF₃H and C₂F₆ are in 10⁻¹² mole cm⁻³ sec⁻¹.

The abstraction of hydrogen by CF₃⁺ was also studied for dimethylamine, dimethylamine-d, and trimethylamine. The results are recorded in Tables 35 to 37 and presented graphically in Figs. 24, 26, 27 and 28. The Arrhenius parameters derived are listed in Table 38, along with those for the corresponding methyl radical reactions.
<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>Me$_2$ND</th>
<th>CF$_3$I</th>
<th>CF$_3$H</th>
<th>CF$_3$D</th>
<th>C$_2$F$_6$</th>
<th>RH</th>
<th>RD</th>
<th>$\frac{1000}{T}$</th>
<th>Log RH</th>
<th>Log RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>370.3</td>
<td>90</td>
<td>0.496</td>
<td>1.00</td>
<td>226</td>
<td>40.8</td>
<td>8.64</td>
<td>155</td>
<td>28.0</td>
<td>2.70</td>
<td>2.190</td>
<td>1.447</td>
</tr>
<tr>
<td>269</td>
<td>370.3</td>
<td>300</td>
<td>0.330</td>
<td>1.01</td>
<td>613</td>
<td>11.2</td>
<td>2.08</td>
<td>129</td>
<td>23.6</td>
<td>2.70</td>
<td>2.111</td>
<td>1.373</td>
</tr>
<tr>
<td>270</td>
<td>370.3</td>
<td>300</td>
<td>0.234</td>
<td>0.817</td>
<td>57</td>
<td>9.1</td>
<td>1.96</td>
<td>174</td>
<td>27.7</td>
<td>2.70</td>
<td>2.244</td>
<td>1.443</td>
</tr>
<tr>
<td>294</td>
<td>370.3</td>
<td>45</td>
<td>0.463</td>
<td>1.12</td>
<td>197</td>
<td>37.5</td>
<td>7.54</td>
<td>155</td>
<td>29.5</td>
<td>2.70</td>
<td>2.190</td>
<td>1.470</td>
</tr>
<tr>
<td>298</td>
<td>357.1</td>
<td>90</td>
<td>0.511</td>
<td>0.765</td>
<td>95</td>
<td>20.7</td>
<td>5.21</td>
<td>81.1</td>
<td>17.8</td>
<td>2.80</td>
<td>1.909</td>
<td>1.250</td>
</tr>
<tr>
<td>301</td>
<td>344.8</td>
<td>90</td>
<td>0.908</td>
<td>0.641</td>
<td>94</td>
<td>18.0</td>
<td>1.59</td>
<td>82.0</td>
<td>15.7</td>
<td>2.90</td>
<td>1.914</td>
<td>1.196</td>
</tr>
<tr>
<td>295</td>
<td>333.3</td>
<td>90</td>
<td>0.338</td>
<td>0.814</td>
<td>75</td>
<td>13.2</td>
<td>7.01</td>
<td>83.1</td>
<td>14.7</td>
<td>3.00</td>
<td>1.920</td>
<td>1.167</td>
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<td>333.3</td>
<td>90</td>
<td>0.791</td>
<td>1.18</td>
<td>85</td>
<td>18.4</td>
<td>3.66</td>
<td>56.2</td>
<td>12.2</td>
<td>3.00</td>
<td>1.750</td>
<td>1.086</td>
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<td>300</td>
<td>322.6</td>
<td>90</td>
<td>1.44</td>
<td>1.01</td>
<td>125</td>
<td>23.3</td>
<td>2.54</td>
<td>54.8</td>
<td>10.2</td>
<td>3.10</td>
<td>1.739</td>
<td>1.009</td>
</tr>
</tbody>
</table>

Me$_2$ND and CF$_3$I are in 10$^{-6}$ mole cm$^{-3}$; CF$_3$H, CF$_3$D and C$_2$F$_6$ in 10$^{-12}$ mole cm$^{-3}$sec$^{-1}$.

RH refers to abstraction from the methyl groups, RD to abstraction from ND.
TABLE 37

Photolysis of TFMI in the Presence of Trimethylamine

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>Me$_3$N</th>
<th>CF$_3$I</th>
<th>CF$_3$H</th>
<th>C$_2$F$_6$</th>
<th>R</th>
<th>$\frac{1000}{T}$</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>303.0</td>
<td>100</td>
<td>0.175</td>
<td>1.76</td>
<td>67.1</td>
<td>18.8</td>
<td>88.5</td>
<td>3.30</td>
<td>1.947</td>
</tr>
<tr>
<td>207</td>
<td>303.5</td>
<td>45</td>
<td>1.01</td>
<td>1.00</td>
<td>390</td>
<td>21.6</td>
<td>83.3</td>
<td>3.30</td>
<td>1.921</td>
</tr>
<tr>
<td>205</td>
<td>322.5</td>
<td>100</td>
<td>0.164</td>
<td>1.65</td>
<td>93.9</td>
<td>14.6</td>
<td>150</td>
<td>3.10</td>
<td>2.176</td>
</tr>
<tr>
<td>206</td>
<td>344.8</td>
<td>100</td>
<td>0.174</td>
<td>1.76</td>
<td>150</td>
<td>14.0</td>
<td>230</td>
<td>2.90</td>
<td>2.362</td>
</tr>
<tr>
<td>210</td>
<td>370.3</td>
<td>45</td>
<td>1.12</td>
<td>1.11</td>
<td>1008</td>
<td>10.6</td>
<td>277</td>
<td>2.70</td>
<td>2.443</td>
</tr>
<tr>
<td>201</td>
<td>400.0</td>
<td>120</td>
<td>0.221</td>
<td>1.19</td>
<td>351</td>
<td>12.5</td>
<td>449</td>
<td>2.50</td>
<td>2.652</td>
</tr>
<tr>
<td>211</td>
<td>400.0</td>
<td>45</td>
<td>0.305</td>
<td>1.25</td>
<td>721</td>
<td>17.3</td>
<td>568</td>
<td>2.50</td>
<td>2.754</td>
</tr>
<tr>
<td>213</td>
<td>434.8</td>
<td>30</td>
<td>0.387</td>
<td>1.59</td>
<td>1215</td>
<td>12.7</td>
<td>879</td>
<td>2.30</td>
<td>2.944</td>
</tr>
<tr>
<td>212</td>
<td>434.8</td>
<td>60</td>
<td>0.266</td>
<td>1.09</td>
<td>684</td>
<td>9.95</td>
<td>815</td>
<td>2.30</td>
<td>2.911</td>
</tr>
</tbody>
</table>

Me$_3$N and CF$_3$I are in 10$^{-6}$ mole cm$^{-3}$;
CF$_3$H and C$_2$F$_6$ in 10$^{-12}$ mole cm$^{-3}$ sec$^{-1}$.

The activation energy requirements for the methyl radical abstractions shown in Table 38 exceed these of CF$_3^-$ by a little over 3 kcal/mole in every case, with little change in $A$.

TABLE 38

TRIFLUOROMETHYL RADICALS   METHYL RADICALS

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>Log A</th>
<th>Log $k_{164}$</th>
<th>E</th>
<th>Log A</th>
<th>Log $k_{164}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$)$_2$NH</td>
<td>5.1</td>
<td>11.8</td>
<td>9.2</td>
<td>8.7</td>
<td>11.5</td>
<td>7.1</td>
<td>83</td>
</tr>
<tr>
<td>(CH$_3$)$_2$NH</td>
<td>3.3</td>
<td>10.5</td>
<td>8.9</td>
<td>6.4</td>
<td>10.8</td>
<td>7.6</td>
<td>&quot;</td>
</tr>
<tr>
<td>(CH$_3$)$_2$ND</td>
<td>4.7</td>
<td>10.9</td>
<td>8.5</td>
<td>7.8</td>
<td>10.7</td>
<td>6.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>(CH$_3$)$_3$N</td>
<td>4.5</td>
<td>11.8</td>
<td>9.5</td>
<td>8.0</td>
<td>12.6</td>
<td>8.6</td>
<td>120,121</td>
</tr>
</tbody>
</table>

E is in kcal/mole, A and $k_{164}$ in mole$^{-1}$cm$^3$sec$^{-1}$.

The hydrogen abstracted is underlined.
FIG. 27. HYDROGEN ABSTRACTION BY CF$_3^\cdot$ RADICALS

Log R

TRIMETHYLAMINE

ETHYLENEIMINE (Overall)

1,000/T

FIG. 28. TEST OF MECHANISM

$\frac{10^{-6}}{R_{C_2F_6}}$

$10^{-6}[RH]/R_{CF_3H}$

○ Trimethylamine at 127°C; ▲ Ethyleneimine at 162°C;
○ Dimethylamine (Overall Abstraction) at 60°C.
For either radical the activation energy for abstraction from the amine site in dimethylamine is around 2 kcal/mole lower than that for abstraction from the methyl groups. On a per-hydrogen atom basis the A-factor for methyl radical abstraction is the same for both sites, while for CF$_3^-$ there is again a suggestion of depression of the A-factor for abstraction from the polar position, although in this case the difference does not exceed the experimental error.

Since the polarity of Me$_2$NH is considerably less than that of CH$_3$NH$_2$ or CH$_3$OH, less pronounced dipole interactions are to be expected. With both radicals, the activation energy for abstraction from the N-D group exceeds that for N-H by 1·4 kcal/mole, in good agreement with the zero-point energy difference of 1·3 kcal/mole.

Gray and Jones (122) have studied the abstraction of hydrogen from ethyleneimine by methyl radicals, and found that attack occurs almost exclusively at the NH position.

### TABLE 39

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>IMINE</th>
<th>CF$_3$I</th>
<th>CF$_3$H</th>
<th>CF$_2$F$_6$</th>
<th>R 1000</th>
<th>T</th>
<th>Log R</th>
</tr>
</thead>
<tbody>
<tr>
<td>284</td>
<td>303.1</td>
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<td>0.429</td>
<td>1.76</td>
<td>57.3</td>
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<td>20.9</td>
<td>3.30</td>
<td>1.320</td>
</tr>
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<td>45</td>
<td>1.95</td>
<td>0.771</td>
<td>110</td>
<td>3.96</td>
<td>28.5</td>
<td>3.10</td>
<td>1.455</td>
</tr>
<tr>
<td>285</td>
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<td>45</td>
<td>0.252</td>
<td>1.00</td>
<td>59.7</td>
<td>21.1</td>
<td>51.5</td>
<td>2.90</td>
<td>1.712</td>
</tr>
<tr>
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<td>370.3</td>
<td>45</td>
<td>0.384</td>
<td>1.58</td>
<td>136</td>
<td>26.9</td>
<td>68.0</td>
<td>2.70</td>
<td>1.833</td>
</tr>
<tr>
<td>287</td>
<td>400.0</td>
<td>90</td>
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<td>2.42</td>
<td>86.3</td>
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<td>434.8</td>
<td>45</td>
<td>0.387</td>
<td>1.59</td>
<td>470</td>
<td>55.2</td>
<td>163</td>
<td>2.30</td>
<td>2.212</td>
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<tr>
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<td>90</td>
<td>0.540</td>
<td>1.03</td>
<td>297</td>
<td>9.19</td>
<td>181</td>
<td>2.30</td>
<td>2.258</td>
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</table>
In the present work the overall kinetics of hydrogen abstraction by trifluoromethyl radicals have been studied (Table 39 and Figs. 27 and 28) and the results are presented in Table 40 along with those for methyl radicals.

**TABLE 40**

\[
\begin{array}{ccc}
\text{CH}_3^* + \overset{\text{CH}}{\text{NH}} & \rightarrow & \text{CH}_4 + \overset{\text{CH}}{\text{NH}} \\
& & 10.1 \\
& \rightarrow & \text{CH}_4 + \overset{\text{C}_2\text{H}_4\text{N}}{\text{N}} \\
& & 4.6 \\
& \rightarrow & \text{CH}_4 + [\text{C}_2\text{H}_4\text{N}]^* \\
\text{CF}_3^* + \overset{\text{CH}}{\text{NH}} & \rightarrow & \text{CF}_3\text{H} + [\text{C}_2\text{H}_4\text{N}]^* \\
& & 4.1 \\
\end{array}
\]

E is in kcal/mole, A and \(\log k_{164}\) in mole\(^{-1}\)cm\(^3\)sec\(^{-1}\)

The Arrhenius parameters recorded in Table 40 strongly suggest that in the case of \(\text{CF}_3^*\) there is appreciable attack at both sites. Both the activation energy and A-factor are higher than would be expected on the basis of the parameters reported by Gray and Jones for attack at the NH group alone, but lower than would be expected for abstraction from \(\text{CH}_2\). A similar effect is observed for dimethylamine, where the ratio \(k_{\text{METHYL}}/k_{\text{AMINO}}\) at 164°C is six times greater for \(\text{CF}_3^*\) attack than it is for methyl radicals. For methyamine the relative rate of attack at the methyl position is about twelve times greater for the polar radical. Once more this may be interpreted in terms of dipole-dipole repulsion, inhibiting attack at the polar site.
CHAPTER 7

As mentioned in Chapter 1, conflicting data have been reported for the photolysis of fluoroaldehydes, interpreted in terms of the following reaction scheme:

\[ R_fCHO + \text{hv} \rightarrow R_f^* + \text{CHO}. \]
\[ R_f^* + R_fCHO \rightarrow R_fH + R_fCO^* \quad (k_a) \]
\[ R_f + R_f \rightarrow R_{f2} \quad (k_c) \quad R_f^* + \text{CO} \]

Arrhenius parameters reported for the hydrogen abstraction reaction are listed below.

<table>
<thead>
<tr>
<th>ALDEHYDE</th>
<th>E</th>
<th>Log A</th>
<th>Log k_{164}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF_3CHO</td>
<td>8.4</td>
<td>11.7</td>
<td>7.5</td>
<td>Dodd and Smith</td>
</tr>
<tr>
<td>C_2F_5CHO</td>
<td>4.5</td>
<td>10.2</td>
<td>7.9</td>
<td>Pritchard et al.</td>
</tr>
<tr>
<td>n-C_3F_7CHO</td>
<td>4.0</td>
<td>9.9</td>
<td>7.9</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

E is in kcal/mole, A and k_{164} in mole^{-1}cm^3sec^{-1}.

On the basis of their work with perfluoropropionaldehyde and perfluorobutyraldehyde, Pritchard, Miller and Foote (15) concluded that the activation energy reported by Dodd and Smith (17) for hydrogen atom abstraction from trifluoroacetaldehyde by CF_3^* was "improbably high".

In the present work the abstraction of hydrogen from these three fluoroaldehydes has been studied with methyl radicals from the thermal decomposition of DTBP and trifluoromethyl radicals generated by photolysis of HFA. (Tables 42 to 47 and Figs. 29 to 40).
<table>
<thead>
<tr>
<th>RUN</th>
<th>T (°K)</th>
<th>t (sec)</th>
<th>ALD</th>
<th>HFA</th>
<th>CF&lt;sub&gt;3&lt;/sub&gt;H</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;6&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;5&lt;/sub&gt;H</th>
<th>C&lt;sub&gt;3&lt;/sub&gt;F&lt;sub&gt;8&lt;/sub&gt;</th>
<th>C&lt;sub&gt;4&lt;/sub&gt;F&lt;sub&gt;10&lt;/sub&gt;</th>
<th>( \Phi )</th>
<th>R</th>
<th>( \frac{1000}{T} )</th>
<th>Log R</th>
</tr>
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ALD and HFA are in \(10^{-6}\) mole cm\(^{-3}\); 
\(\text{CF}_3\text{H}, \text{C}_2\text{F}_6, \text{C}_2\text{F}_5\text{H}, \text{C}_3\text{F}_8\) and \(\text{C}_4\text{F}_{10}\) are in \(10^{-12}\) mole cm\(^{-3}\) sec\(^{-1}\).
### TABLE 43.

Photolysis of HFA/\(C_3F_7CHO\) Mixtures

<table>
<thead>
<tr>
<th>RUN</th>
<th>(T(°K))</th>
<th>(t(\text{sec}))</th>
<th>ALD.</th>
<th>HFA</th>
<th>(\text{CF}_3\text{H})</th>
<th>(\text{C}_2\text{F}_6)</th>
<th>R</th>
<th>(\frac{1000}{T})</th>
<th>Log R</th>
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<tbody>
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<td>71.5</td>
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<td>1.90</td>
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<td>1.355</td>
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<td>11.9</td>
<td>2.30</td>
<td>1.074</td>
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<td>2.50</td>
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<td>100</td>
<td>0.737</td>
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<td>31.9</td>
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<td>6.61</td>
<td>2.50</td>
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<td>0.884</td>
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</table>

ALD. and HFA are in \(10^{-6}\) mole cm\(^{-3}\)

\(\text{CF}_3\text{H}\) and \(\text{C}_2\text{F}_6\) are in \(10^{-12}\) mole cm\(^{-3}\)sec\(^{-1}\).
### TABLE 44.

Photolysis of HFA/CF₃CHO Mixtures

<table>
<thead>
<tr>
<th>RUN</th>
<th>T(°K)</th>
<th>t(sec)</th>
<th>ALD.</th>
<th>HFA</th>
<th>CF₃H</th>
<th>C₂F₆</th>
<th>R</th>
<th>( \frac{1000}{T} )</th>
<th>Log R</th>
</tr>
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<tbody>
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ALD. and HFA are in \( 10^{-6} \) mole cm\(^{-3} \),
CF₃H and C₂F₆ in \( 10^{-12} \) mole cm\(^{-3} \) sec\(^{-1} \).

The runs performed at 400 and 417°c were not included in the least-squares calculation of Arrhenius Parameters.
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<th>CH₄</th>
<th>C₂H₆</th>
<th>R</th>
<th>1000/T</th>
<th>Log R</th>
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<th>C₂H₆</th>
<th>R</th>
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Units as in Table 47.
TABLE 46.
Thermal-Decomposition of DTBP in the Presence of Perfluoropropionaldehyde

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<th>T(°K)</th>
<th>t(sec)</th>
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<th>CH₄</th>
<th>C₂H₆</th>
<th>R</th>
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<th>Log R</th>
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Units as in Table 47.
### TABLE 47

Thermal Decomposition of DTBP in the Presence of Perfluorobutyraldehyde

<table>
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<th>t (sec)</th>
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<th>DTBP</th>
<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
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<th>1000/T</th>
<th>Log R</th>
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ALD. and DTBP are in 10$^{-6}$ mole cm$^{-3}$, CH$_4$ and C$_2$H$_6$ in 10$^{-12}$ mole cm$^{-3}$sec$^{-1}$.  

CH$_4$, the rate of formation of methane, has been corrected for the contribution arising by abstraction from the radical source, and refers only to abstraction from CHO.
PHOTOLYSIS OF DTBP IN THE PRESENCE OF FLUOROALDEHYDES

**FIG. 29.** $\text{CH}_3^- + \text{CF}_3 \text{CHO} \rightarrow \text{CH}_4 + \text{CF}_3 \text{CO}^-$

![Graph showing the reaction between $\text{CH}_3^- + \text{CF}_3 \text{CHO}$ and the products $\text{CH}_4 + \text{CF}_3 \text{CO}^-$.]

**FIG. 30.** $\text{CH}_3^- + \text{C}_2\text{F}_5 \text{CHO} \rightarrow \text{CH}_4 + \text{C}_2\text{F}_5 \text{CO}^-$

![Graph showing the reaction between $\text{CH}_3^- + \text{C}_2\text{F}_5 \text{CHO}$ and the products $\text{CH}_4 + \text{C}_2\text{F}_5 \text{CO}^-$.]

**FIG. 31.** $\text{CH}_3^- + \text{n-C}_3\text{F}_7 \text{CHO} \rightarrow \text{CH}_4 + \text{n-C}_3\text{F}_7 \text{CO}^-$

![Graph showing the reaction between $\text{CH}_3^- + \text{n-C}_3\text{F}_7 \text{CHO}$ and the products $\text{CH}_4 + \text{n-C}_3\text{F}_7 \text{CO}^-$.]
PHOTOLYSIS OF HFA/C2F5CHO MIXTURES
- Test of Mechanism for CF3H Formation -

\[ \frac{10^6 R_{CF_3H}}{R_{C_2F_6}} \]

FIG. 32.

\[ 10^6 [ALD] \]

O - 500°K;  ● - 400°K.
PHOTOLYSIS OF HFA/C$_2$F$_5$CHO MIXTURES.

- Test of Mechanism for C$_2$F$_5$H Formation -

FIG. 33.

$\frac{10^6 R_{C_2F_5H}}{R_{C_4F_{10}}} = f(10^6 [ALD])$

○ - 500°K; ○ - 400°K
PHOTOLYSIS OF $\text{C}_2\text{F}_5\text{CHO}$ (AT $302 \pm 3^\circ\text{K}$)

From Results Published by Pritchard, Miller and Foote (Ref. 15)

TEST OF MECHANISM FOR $\text{C}_2\text{F}_5\text{H}$ FORMATION

![Graph showing the relationship between $10^6 \frac{R_{C_2F_5H}}{R_{C_4F_{10}}}$ and $10^6 [\text{ALD}]$.]
From Figs. 32 and 33 it is evident that while fluoroform produced on photolysis of mixtures of HFA and \( \text{C}_2\text{F}_5\text{CHO} \) may be accounted for by the reactions
\[
\text{CF}_3^- + \text{C}_2\text{F}_5\text{CHO} \rightarrow \text{CF}_3\text{H} + \text{C}_2\text{F}_5\text{CO}^- \quad (k_a)
\]
and
\[
\text{CF}_3^- + \text{CF}_3^- \rightarrow \text{C}_2\text{F}_6 \quad (k_c)
\]
the pentafluoroethane formation cannot be explained solely in terms of the corresponding reactions of the perfluoroethyl radical. Analysis of published data (13) for the photolysis of \( \text{C}_2\text{F}_5\text{CHO} \) supports this conclusion (Fig. 34). It is suggested that \( \text{C}_2\text{F}_5\text{H} \) is formed intramolecularly as a primary photolytic process, so that the reactions leading to measured products are:

\[
\text{R}_f\text{CHO} + \text{hv} \rightarrow \begin{cases} \text{R}_f\text{H} + \text{CO} & \text{(I)} \\ \text{R}_f^- + \text{CHO}^- & \text{(II)} \end{cases}
\]

\[
\begin{aligned}
\text{CF}_3^- + \text{R}_f\text{CHO} & \rightarrow \text{CF}_3\text{R}_f^- + \text{R}_f\text{CO}^- \\
\text{R}_f^- + \text{R}_f\text{H} + \text{R}_f\text{CO}^- & \rightarrow \text{R}_f^- + \text{CO} \\
& \text{(Chain)}
\end{aligned}
\]

\[
\text{CF}_3^- + \text{R}_f^- \rightarrow \text{CF}_3\text{R}_f^- \quad \text{R}_f^- + \text{R}_f \rightarrow \text{R}_f^2
\]

The observed cross-combination ratio for \( \text{C}_2\text{F}_5^- \) and \( \text{CF}_3^- \) was \( 2.0 \pm 0.1 \), (Independent of Temperature).

At low temperatures Pritchard and his colleagues observed a wide scatter of values of \( R \); this may be explained in terms of the greater relative importance of the intramolecular formation of \( \text{C}_2\text{F}_5\text{H} \) for low values of \( k_a \), shown in Fig. 33.
By raising disproportionately the apparent value of \( k_a \) at low temperatures, the occurrence of reaction I will lead to low Arrhenius parameters for the abstraction reaction, as found by Pritchard.

As a further test of the above reaction scheme, a few runs were performed in which \( C_2F_2CHO \) was photolysed in the presence of nitric oxide, perfluoroethyl radicals being removed from the system by the reaction

\[
C_2F_5^+ + NO \rightarrow C_2F_5NO
\]

While \( C_4F_{10} \) formation was inhibited completely, \( C_2F_5H \) was detected in appreciable amounts. In a typical inhibited run at 4000 K the \( C_2F_5H \) yield was 25% of that for comparable runs without NO. Similar results were observed for \( CF_3CHO \) and \( C_3F_7CHO \). Since in unscavenged runs decarbonylation of \( R_fCO^* \) is likely to be the principal source of \( R_f^* \), this relatively low degree of \( R_fH \) inhibition indicates that reaction I is at least comparable with II as a mode of photodecomposition of \( R_fCHO \). In the case of trifluoroacetaldehyde it is not possible to distinguish between \( CF_3H \) arising from abstraction and that formed intramolecularly. Although high relative concentrations of HFA were used, distinct curvature of the Arrhenius plot was observed below 150°C, (Fig. 35), as found by Dodd and Smith for photolysis of the aldehyde alone, while even at 280°C there is evidence (Figs. 36 and 37) that the intramolecular reaction is contributing significantly to the total yield of fluoroform.
PHOTOLYSIS OF HFA/CF₃CHO MIXTURES: ARRHENIUS PLOT

All Fluoroform is attributed to the Reaction:

\[ \text{CF}_3^- + \text{CF}_3\text{CHO} \rightarrow \text{CF}_3\text{H} + \text{CF}_3\text{CO}^- \]
PHOTOLYSIS OF HFA/CF₃CHO MIXTURES (AT 556°K)
- Test of Mechanism of CF₃H Formation -

**FIG. 36.**

\[ \frac{10^6 R_{CF_3H}}{R_{C_2F_6}} \]

\[ \frac{10^6[ALD]}{10^6[ALD]} \]

PHOTOLYSIS OF CF₃CHO (AT 556°K)
- Test of Mechanism of CF₃H Formation -

**FIG. 37.**

\[ \frac{10^6 R_{CF_3H}}{R_{C_2F_6}} \]

\[ \frac{10^6[ALD]}{10^6[ALD]} \]
PHOTOLYSIS OF HFA/C$_2$F$_5$CHO MIXTURES: ARRHENIUS PLOT FOR:

\[ \text{CF}_3 \cdot + \text{C}_2\text{F}_5\text{CHO} \rightarrow \text{CF}_3\text{H} + \text{C}_2\text{F}_5\text{CO}. \]

**FIG. 38.**

![Graph showing an Arrhenius plot with log R on the y-axis and 1,000/T on the x-axis. The graph is a straight line with data points.]
PHOTOLYSIS OF HFA/C$_3$F$_7$CHO MIXTURES: ARRHENIUS PLOT FOR:

CF$_3$ + C$_3$F$_7$CHO → CF$_3$H + C$_3$F$_7$CO.

Log R vs. 1000/T
PHOTOLYSIS OF HFA/C\textsubscript{3}F\textsubscript{7}CHO MIXTURES.

TEST OF MECHANISM

\[ C_{3}F_{7}CHO + CF_{3} \rightarrow C_{3}F_{7}CO + CF_{3}H \]

\[ CF_{3} + CF_{3} \rightarrow C_{2}F_{6} \]

FIG. 40.
Arrhenius parameters calculated for the substantially linear portion of the plot above 150°C are in excellent agreement with those reported by Dodd and Smith.

\[
\begin{align*}
E & \quad \log A & \quad \log k_{164} \\
8.4 & \quad 11.7 & \quad 7.5 & \quad \text{Dodd and Smith.} \\
8.8 & \quad 12.0 & \quad 7.6 & \quad \text{This Work.}
\end{align*}
\]

E is in kcal/mole, A and \(k_{164}\) in \text{mole}^{-1}\text{cm}^3\text{sec}^{-1}.

In view of the uncertainty which in this case exists over the relative importance of intramolecular elimination, these parameters should not be regarded as entirely reliable. No such uncertainty, of course, exists in the case of \(\text{CF}_3^-\) attack on higher perfluoroaldehydes. The Arrhenius parameters obtained for these reactions are listed in Table 48, together with the parameters obtained for methyl radical attack on perfluoroaldehydes. For purposes of comparison, Arrhenius parameters are also included for abstraction from normal aldehydes. The activation energy for abstraction of an aldehydic hydrogen atom by \(\text{CF}_3^-\) appears to be around 3.5 kcal/mole lower than that for \(\text{CH}_3^-\), in good agreement with the value established by Pritchard (77). It is evident from Table 48 that the Arrhenius parameters for radical attack on \(\text{RCHO}\) increase as the complexity of \(\text{R}\) increases, in the order

\[
\text{H} < \text{Me} < \text{CF}_3 < \text{i-Pr} < \text{C}_2\text{F}_5 < \text{t-Bu} < \text{n-C}_3\text{F}_7,
\]

although \(\log k_{164}\) remains essentially constant at 8.0 ± 0.2 (\(k\) is in \text{mole}^{-1}\text{cm}^3\text{sec}^{-1}), except for formamide which reacts more slowly by a factor of ten.
<table>
<thead>
<tr>
<th></th>
<th>Methyl Radicals</th>
<th>Trifluoromethyl Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
<td>Log A</td>
</tr>
<tr>
<td>CF$_3$CHO</td>
<td>8.7</td>
<td>12.1</td>
</tr>
<tr>
<td>C$_2$F$_5$CHO</td>
<td>9.8</td>
<td>12.9</td>
</tr>
<tr>
<td>n-C$_3$F$_7$CHO</td>
<td>10.3</td>
<td>13.2</td>
</tr>
<tr>
<td>HCHO</td>
<td>6.6</td>
<td>10.3</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>7.6</td>
<td>11.9</td>
</tr>
<tr>
<td>i-C$_3$H$_7$CHO</td>
<td>8.7</td>
<td>12.6</td>
</tr>
<tr>
<td>t-C$_4$H$_9$CHO</td>
<td>10.2</td>
<td>13.0</td>
</tr>
<tr>
<td>n-C$_4$H$_9$CHO</td>
<td>8.0</td>
<td>12.1</td>
</tr>
</tbody>
</table>

$E$ is in kcal/mole, $A$ and $k_{164}$ in mole$^{-1}$cm$^2$sec$^{-1}$. (p - This Work)
For normal aldehydes Trotman-Dickinson has suggested that the observed variation in Arrhenius parameters is spurious (153), and has attributed it to experimental error. However, since the same general trend is observed for fluoroaldehydes, formates and formamides (126, 127, 128, 129) this explanation seems rather unsatisfactory, especially since in many cases the variation involved is considerably outwith any reasonable estimate of likely experimental error. It should also be noted that the A-factors observed for the more complex aldehydes are far higher than have been reported for any other hydrogen abstractions. The following tentative explanation of these observations is suggested.

It is well established (59, 130, 131) that free radicals will readily associated with the electrons of a double bond to form a Π-complex, this being the first stage in the addition of radicals to unsaturated molecules. Szwarc (59, 131) has suggested that this process occurs with zero activation energy. The stability of such complexes has been demonstrated by E.S.R. studies (130). It would therefore seem possible that the principal mode of radical attack involves the carbonyl group rather than the hydrogen atom, with subsequent intramolecular elimination of RH.

\[ \text{Reactants} \quad \Pi\text{-complex} \quad \text{Activated complex} \quad \text{Products} \]

\[ R'-C=O + R' \rightarrow R'-C=O \quad \rightarrow \quad R'-C=O \quad \rightarrow \quad R-C. + HR \]
The probability of transition to the activated complex must evidently depend upon the life-time of the Π-complex, which in turn must depend on the availability of oscillators capable of removing energy from the reactive centre. This may be correlated with the observed A-factors for the reaction: CH₃⁺ + R'CHO → CH₄ + R'CO⁺.

R': H Me Et n-Pr n-Bu Me₂CH Me₃C
Log A: 10.3 11.9 12.0 11.8 12.1 12.6 13.0

Comparison of the values for n-propyl and i-propyl, and for n-butyl and t-butyl, suggests that the number of carbon-carbon oscillators adjacent to the aldehyde group is of importance, rather than the size of the alkyl group. This is further illustrated by the observed A-factors for CH₃, C₂H₅, n-C₃H₇ and n-C₄H₉ where no systematic variation occurs, and is shown graphically in Fig. 41. As the number of available oscillators of suitable frequency for near-resonance transfer of energy from the reactive centre increases, log A appears to approach the value of around 13.4, found for radical combination. In view of the likelihood that Π-complex formation and radical combination both have zero activation energy, it is not unreasonable to suggest that the two will take place at comparable rates. If this is the case, then Fig. 41 indicates that with increasing stability of the Π-complex the probability of ultimate successful transition to the activated complex approaches unity for systems possessing the necessary energy indicated in Fig. 42.
\[ \text{RCHO} + \text{CH}_3^* \rightarrow \text{RCO}^* + \text{CH}_4 \]

**FIG. 41.**

<table>
<thead>
<tr>
<th>C-Me Bonds</th>
<th>Log A</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCHO</td>
<td>0</td>
</tr>
<tr>
<td>MeCHO</td>
<td>1</td>
</tr>
<tr>
<td>Me_2CHCHO</td>
<td>2</td>
</tr>
<tr>
<td>Me_3CCHO</td>
<td>3</td>
</tr>
</tbody>
</table>

**FIG. 42.**

Transition State

\[
\text{P.E.} \\
\text{RCHO + Rad}^* \\
\pi-\text{Complex} \\
\text{E} \\
\text{RCO}^* + \text{RadH} \\
\text{Reaction Co-Ordinate}
\]
It is evident that the energy required will increase with increasing well-depth, i.e. with increasing stability of the \( \pi \)-complex, which is in accord with the observed trend in activation energies from HCHO to t-BuCHO. Extending this treatment to formates and formamides, it would be reasonable to expect a decrease in stability of the \( \pi \)-complex (and consequent decrease in A-Factor for abstraction) due to withdrawal of \( \pi \)-electrons, in the order:

\[
\begin{align*}
-\text{O}=\text{C}=\text{O} & \quad \text{N}=\text{C}=\text{O} & \quad \text{C}=\text{C}=\text{O} \\
\text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

This is in fact found to be the case, as is shown in Fig. 43 where Log A is plotted against the Pauling electronegativity of the atom adjacent to the carbonyl group. Similar destabilisation of the \( \pi \)-complex by electron withdrawal is shown by the lower Arrhenius parameters for attack by the highly electronegative CF\(_3\) radicals relative to those for CH\(_3\)\.

While the proposed mechanism is, of course, highly speculative, it appears to provide a cohesive explanation of the observed variations in the Arrhenius parameters for hydrogen abstraction from RCHO brought about by changes in R, and also to account for the extremely high A-factors for abstraction from complex aldehydes.

In the course of this work an attempt was made to study the kinetics of hydrogen abstraction by CF\(_3\) from non-fluorinated aldehydes. A few preliminary runs were
In Fig. 43, Log A for the Reaction

\[ RXCHO + CF_3 \cdot \rightarrow RXCO^- + CF_3H \]

is plotted against the Electronegativity of the Atom X, adjacent to the CHO group.

In order to keep the effects of energy transfer as constant as possible the compounds considered are:

- **Ethyl Formate**: \( C_2H_5OCHO \)  
  Log A: 10.5  
  E: 8.2

- **Dimethyl Formamide**: \( C_2H_6NCHO \)  
  Log A: 11.4  
  E: 8.3

- **Isobutyraldehyde**: \( C_2H_7CCHO \)  
  Log A: 12.6  
  E: 8.7

**Pauling Electronegativities**

- C: 2.5
- N: 3.0
- O: 3.5
performed in which HFA was photolysed in the presence or propionaldehyde, the results being interpreted in terms of the following reactions:

\[
\begin{align*}
{\text{CF}_3^\cdot} + {\text{C}_2\text{H}_5\text{CHO}} & \rightarrow {\text{CF}_3\text{H}} + {\text{C}_2\text{H}_5\text{CO}^\cdot} \\
{\text{C}_2\text{H}_5^\cdot} + {\text{C}_2\text{H}_5^\cdot} & \rightarrow {\text{C}_2\text{H}_6} + {\text{C}_2\text{H}_6} + \text{CO} \\
{\text{C}_2\text{H}_5^\cdot} + {\text{C}_2\text{H}_5\text{CHO}} & \rightarrow {\text{C}_2\text{H}_6} + {\text{C}_2\text{H}_5\text{CO}^\cdot} \\
{\text{CF}_3^\cdot} + {\text{CF}_3^\cdot} & \rightarrow {\text{C}_2\text{F}_6} \\
{\text{C}_2\text{H}_5^\cdot} + {\text{C}_2\text{H}_5^\cdot} & \rightarrow {\text{C}_2\text{H}_5\text{CF}_3}
\end{align*}
\]

It was immediately evident, however, that this scheme was not obeyed. While the disproportion/combination ratio for ethyl radicals is ~1.14, values of \( \frac{R_{\text{C}_2\text{H}_4}}{R_{\text{C}_4\text{H}_{10}}} \) ranged from ~0.02 to ~4.5, while the cross-combination ratio for \( {\text{C}_2\text{H}_5^\cdot} \) and \( {\text{CF}_3^\cdot} \) varied with temperature between 3·3 and 4·5. Values calculated for \( R \) at constant temperature showed marked make-up dependence. To explain these observations the following additional reactions are proposed.

\[
\begin{align*}
{\text{C}_2\text{H}_5^\cdot} + {\text{CF}_3^\cdot} & \rightarrow {\text{C}_2\text{H}_4} + \text{CF}_3\text{H} \\
{\text{C}_2\text{H}_4\text{CF}_3^\cdot} & \rightarrow {\text{C}_2\text{H}_5\text{CF}_3} + {\text{C}_2\text{H}_4} \\
{\text{C}_2\text{H}_5\text{CHO}} & \rightarrow {\text{C}_2\text{H}_5\text{CF}_3} + {\text{C}_2\text{H}_5\text{CO}^\cdot}
\end{align*}
\]

Recently it has been shown that the addition of \( {\text{CF}_3^\cdot} \) to ethylene occurs over 1,000 times more rapidly than
addition of \( \text{CH}_3^- \) (61), while the C-H bond strength in \( \text{CF}_3H \) is likely to make disproportionation with alkyl radicals a more important mode of reaction for \( \text{CF}_3^- \) than it is for \( \text{CH}_3^- \). Since ethylene is formed by one of these reactions and removed by the other, the fluctuating values observed for the yield of ethylene relative to that of butane are explained. The observed high, temperature dependent, values calculated for the cross-combination ratio may also be explained in terms of the formation of additional \( \text{C}_2\text{H}_5\text{CF}_3 \) by the reactions indicated.

As a test of this mechanism HFA was photolysed in the presence of ethane, ethyl radicals being formed by abstraction. Similar results were observed. It seems probable that similar complications occur whenever alkyl radicals (other than methyl) react with perfluoroalkyl radicals, invalidating the reported cross-combination and disproportionation/combination ratios for such systems.
CHAPTER 8

POLARITY EFFECTS

In previous chapters the effect of dipole-dipole interactions upon the kinetics of hydrogen atom abstraction has been discussed. In Table 49 Arrhenius parameters for the reaction

$$\text{CF}_3^- + \text{RH} \rightarrow \text{CF}_3^- + \text{R}^-$$

are listed in order of decreasing electronegativity of R. While $A$ increases steadily by a factor of almost 1000 on going from methanol to trimethylsilane, there is no such systematic variation in $E$.

<table>
<thead>
<tr>
<th>RH</th>
<th>Log A</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>9.5</td>
<td>3.2</td>
</tr>
<tr>
<td>MeNH$_2$</td>
<td>9.9</td>
<td>4.4</td>
</tr>
<tr>
<td>Me$_2$NH</td>
<td>10.5</td>
<td>3.3</td>
</tr>
<tr>
<td>SH$_2$</td>
<td>11.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Me$_3$CH</td>
<td>11.3</td>
<td>5.3</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>11.9</td>
<td>5.1</td>
</tr>
<tr>
<td>Me$_3$SiH</td>
<td>12.3</td>
<td>5.5</td>
</tr>
</tbody>
</table>

$E$ is in kcal/mole, $A$ in mole$^{-1}$cm$^3$sec$^{-1}$.

The hydrogen abstracted is shown on the right of the formula

It will be observed that the $A$-factor reported by Kale and Timmons (71) for the reaction

$$\text{CF}_3^- + H_2S \rightarrow \text{CF}_3^- + \text{SH}^-$$
fits smoothly into this series. A similar trend is observed for reactions of the type:

\[ \text{CF}_3^- + \text{RCH}_3 \rightarrow \text{CF}_3\text{H} + \text{RCH}_2^- \]

Here it should be possible to observe the effects of dipole interactions more specifically, since in each case the hydrogen abstracted is bonded to a saturated carbon atom. In Fig. 41 Log A is plotted against the dipole moment of RCH\textsubscript{3}. (In the case of trimethylamine the component of the dipole moment along each N-Me bond is taken so that a realistic comparison may be made with methanol and methylamine.)

<table>
<thead>
<tr>
<th></th>
<th>SiMe\textsubscript{4}</th>
<th>NMe\textsubscript{3}</th>
<th>MeNH\textsubscript{2}</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log A</td>
<td>12.0</td>
<td>11.8</td>
<td>10.7</td>
<td>10.0</td>
</tr>
<tr>
<td>E</td>
<td>7.6</td>
<td>4.5</td>
<td>4.2</td>
<td>4.7</td>
</tr>
<tr>
<td>(\mu)</td>
<td>0</td>
<td>0.67</td>
<td>1.26</td>
<td>1.70</td>
</tr>
</tbody>
</table>

E is in kcal/mole, A in mole\(^{-1}\)cm\(^3\)sec\(^{-1}\), \(\mu\) in e.s.u. \(\times 10^\text{18}\).

Again there appears to be a marked lowering of A-factor for CF\textsubscript{3}\(^-\) attack on possible sites, but no systematic variation in activation energy.

\[
\begin{array}{c c c c}
\text{R} - & \text{CH}_3 & \leftrightarrow & \text{CF}_3 \\
\hline
\text{-} & \text{+} & \leftrightarrow & \text{+} \text{-}
\end{array}
\]

In previous chapters this effect has been attributed to relatively long-range electrostatic forces deflecting in incoming CF\textsubscript{3}\(^-\) radical away from +ve. molecular sites, and towards -ve. sites. Such an explanation is, of course, tenable only if CF\textsubscript{3}\(^-\) possesses a dipole moment, which would not
VARIATION WITH DIPOLE MOMENT
OF RCH$_3$ OF LOG A FOR THE REACTION: $\text{RCH}_3 + \text{CF}_3 \rightarrow \text{RCH}_2 + \text{CF}_3\text{H}$

FIG. 44.
be the case if the radical exists preferentially in a planar configuration. Theoretical predictions from electron orbital calculations (153) suggest a non-planar structure, and this is confirmed by E.S.R. studies (134), which show that at 85°K the radical is virtually tetrahedral. While this cannot be taken as conclusive proof that the same configuration will be adopted at the considerably higher temperatures involved in gas-phase kinetic studies, the balance of probabilities appears strongly to favour a planar structure.

While it is generally agreed that hydrogen atoms in positive sites show enhanced resistance to $\text{CF}_3^-$ attack, the origin of this effect has not been conclusively established. The results obtained in the present work suggest that dipole-dipole interactions lower the probability of collision, and hence the A-factor, but that the forces involved are small in comparison with the activation energy for abstraction, $E_{\text{CH}_3} - E_{\text{CF}_3}$ being close to 3 kcal/mole for each of the substrates studied. Other workers however, have reported low or even negative values for this difference in activation energies for abstraction from polar molecules.

The first three compounds listed in Table 51 trifluoroacetaldehyde, dimethylformamide and methyl formate all involve abstraction from the CHO group. If the mechanism proposed in Chapter 7 is valid, then abnormal activation energies are to be expected, since the mode of attack is different from that involved in normal hydrogen abstractions.
The complications mentioned in Chapter 6 appear to invalidate the parameters reported for hydrogen abstraction from ammonia by \( CF_3^- \), probably due to the formation in the initial abstraction process of a small radical with unshared electron pairs available for bonding. It seems likely that the conflicting kinetic data reported for \( CF_3^- \) attack on hydrogen sulphide may result from similar complications. Until a fuller investigation of these two systems has been carried out, it would be unwise to attach too much significance to the parameters reported.

### Table 51

<table>
<thead>
<tr>
<th>Methyl Radicals</th>
<th>E</th>
<th>Log A</th>
<th>Ref</th>
<th>Trifluoromethyl Radicals</th>
<th>E</th>
<th>Log A</th>
<th>Ref</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Me}_2\text{NCHO} )</td>
<td>8·3</td>
<td>11·4</td>
<td>129</td>
<td>( \text{CF}_3\text{CHO} )</td>
<td>7·4</td>
<td>12·1</td>
<td>135</td>
<td>0·9</td>
</tr>
<tr>
<td>( \text{CF}_3\text{CHO} )</td>
<td>8·7</td>
<td>12·1</td>
<td>p</td>
<td>( \text{MeOCHO} )</td>
<td>8·6</td>
<td>11·9</td>
<td>a</td>
<td>0·1</td>
</tr>
<tr>
<td>( \text{MeOCHO} )</td>
<td>9·9</td>
<td>11·2</td>
<td>84</td>
<td>( \text{H}_2\text{S} )</td>
<td>8·7</td>
<td>11·4</td>
<td>84</td>
<td>1·2</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>3·1</td>
<td>11·8</td>
<td>c</td>
<td>( \text{NH}_3 )</td>
<td>4·2</td>
<td>11·8</td>
<td>116</td>
<td>-1·1</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>9·8</td>
<td>10·8</td>
<td>82</td>
<td>( \text{HCl} )</td>
<td>8·3</td>
<td>10·6</td>
<td>119</td>
<td>1·5</td>
</tr>
<tr>
<td>( \text{HCl} )</td>
<td>4·4</td>
<td></td>
<td></td>
<td></td>
<td>5·3</td>
<td>11·4</td>
<td>116</td>
<td>-0·9</td>
</tr>
</tbody>
</table>

E is in kcal/mole, A in mole\(^{-1}\)cm\(^3\)sec\(^{-1}\).

- a - Average of results from Ref. 17 and this work.
- b - Calculated thermochemically from results of Ref. 138.
- c - Average of results from Refs. 136 and 137.
- p - This work.

The remaining parameters given in Table 51, (for the reaction \( CF_3^- + \text{HCl} \rightarrow CF_3\text{H} + \text{Cl}^- \)) are in good agreement with those reported by Whittle, who with various
co-workers has studied hydrogen abstraction by trifluoromethyl radicals from a large number of halogen-containing compounds. The results of this work are summarised in Table 52.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
<td>Log A</td>
<td>Log $k_{164}$</td>
</tr>
<tr>
<td>HCl</td>
<td>5.1</td>
<td>11.2</td>
<td>8.6</td>
</tr>
<tr>
<td>HBr</td>
<td>2.9</td>
<td>11.8</td>
<td>10.3</td>
</tr>
<tr>
<td>HI</td>
<td>0.5</td>
<td>11.7</td>
<td>11.4</td>
</tr>
<tr>
<td>CH$_3$F</td>
<td>11.2</td>
<td>12.1</td>
<td>6.5</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>10.6</td>
<td>12.1</td>
<td>6.8</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>10.4</td>
<td>12.0</td>
<td>6.8</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>7.5</td>
<td>10.6</td>
<td>6.8</td>
</tr>
<tr>
<td>CH$_2$F$_2$</td>
<td>11.2</td>
<td>11.9</td>
<td>6.3</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>7.6</td>
<td>11.2</td>
<td>7.4</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>6.6</td>
<td>11.0</td>
<td>7.7</td>
</tr>
<tr>
<td>CH$_3$CF$_3$</td>
<td>15.8</td>
<td>12.9</td>
<td>5.0</td>
</tr>
<tr>
<td>CF$_2$HCF$_3$</td>
<td>11.5</td>
<td>11.3</td>
<td>5.5</td>
</tr>
<tr>
<td>CF$_2$HCF$_2$H</td>
<td>12.4</td>
<td>12.0</td>
<td>5.8</td>
</tr>
<tr>
<td>(CH$_3$CH$_3$)</td>
<td>8.4</td>
<td>11.7</td>
<td>7.5</td>
</tr>
</tbody>
</table>

$F$ is in kcal/mole, $A$ and $k_{164}$ in mole$^{-1}$cm$^3$sec$^{-1}$.

Although $k_{164}$ for abstraction from related compounds decreases with increasing polarity, there is no suggestion
of the variations in A-factor found in the present work. Indeed, the highest A-factor reported is for the substrate in which hydrogen occupies the most strongly positive site:

\[
\text{CF}_3\text{CH}_3 \rightleftharpoons \cdot\text{CF}_3
\]

The reason for this discrepancy is not clear.

**ABSTRACTION OF HYDROGEN FROM FLUOROFORM**

As outlined in Chapter 1, it is possible to calculate Arrhenius parameters for the reaction

\[ R^* + \text{CF}_3\text{H} \rightarrow \text{RH} + \cdot\text{CF}_3 \]

from the measured parameters for hydrogen abstraction from RH by \( \cdot\text{CF}_3 \). In Table 53 calculated Arrhenius parameters are listed for hydrogen abstraction from methane and fluoroform by \( \text{CH}_3\text{O}^* \) and \( \text{CH}_3\text{NH}^* \) radicals, together with the corresponding parameters for the highly reactive phenyl radical, and the considerably less reactive bromine atom.

<table>
<thead>
<tr>
<th>( R )</th>
<th>( \text{D}(R-H) )</th>
<th>( E )</th>
<th>( \log A )</th>
<th>( \text{Ref} )</th>
<th>( E )</th>
<th>( \log A )</th>
<th>( \text{Ref} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_5^- )</td>
<td>112</td>
<td>5.2</td>
<td>9.9</td>
<td>147</td>
<td>7.5</td>
<td>10.9</td>
<td>147</td>
</tr>
<tr>
<td>( \text{CH}_3\text{O}^- )</td>
<td>102</td>
<td>7.2</td>
<td>9.5</td>
<td>r</td>
<td>8.8</td>
<td>11.1</td>
<td>r</td>
</tr>
<tr>
<td>( \text{CH}_3\text{NH}^- )</td>
<td>93</td>
<td>18.4</td>
<td>9.9</td>
<td>r</td>
<td>15.8</td>
<td>10.4</td>
<td>r</td>
</tr>
<tr>
<td>( \text{Br}^- )</td>
<td>87</td>
<td>22.0</td>
<td>13.0</td>
<td>148</td>
<td>18.2</td>
<td>13.2</td>
<td>149</td>
</tr>
</tbody>
</table>

\( E \) and \( D \) are in kcal/mole, \( A \) in mole\(^{-1}\)cm\(^3\)sec\(^{-1}\).

\( r \) - Calculated from reverse parameters.

The following thermochemical data were used in calculating the reverse parameters.
BOND DISSOCIATION ENERGIES 
(kcal/mole) Ref. 
D(CH$_3$-H) = 104 141 
D(CF$_3$-H) = 106 141 
D(CH$_3$O-H) = 102 142 
D(CH$_3$NH-H) = 93 143 

**ALSO**

D(C$_6$H$_5$-H) = 112 3 
D(Br-H) = 87 4 

<table>
<thead>
<tr>
<th>Bond Dissociation Energies</th>
<th>Entropies of Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(kcal/mole)</td>
<td>Ref.</td>
</tr>
<tr>
<td>D(CH$_3$-H)</td>
<td>104</td>
</tr>
<tr>
<td>D(CF$_3$-H)</td>
<td>106</td>
</tr>
<tr>
<td>D(CH$_3$O-H)</td>
<td>102</td>
</tr>
<tr>
<td>D(CH$_3$NH-H)</td>
<td>93</td>
</tr>
<tr>
<td>D(CH$_3$OH)</td>
<td>56.5</td>
</tr>
</tbody>
</table>

For the reaction $\text{CF}_3^· + \text{RH} \xrightarrow{k_f} \xrightarrow{k_r} \text{CF}_3 \text{H} + \text{R}^·$ 

$\Delta H = E_f - E_r = D(\text{CF}_3^· - \text{H}) - D(\text{R-H}) = 106 - D(\text{R-H})$ kcal/mole 

$\Delta S = \left[ S_{298}^°(\text{CF}_3\text{H}) - S_{298}^°(\text{RH}) \right] + \left[ S_{298}^°(\text{R}^·) - S_{298}^°(\text{CF}_3^·) \right] 
\quad = 1.3 - \left[ S_{298}^°(\text{RH}) - S_{298}^°(\text{R}^·) \right]$ cal. deg$^{-1}$mole$^{-1}$. 

Similarly for $\text{CH}_3^· + \text{RH} \xrightarrow{k_f} \xrightarrow{k_r} \text{CH}_4 + \text{R}^·$ 

$\Delta H = 104 - D(\text{R-H})$ and $\Delta S = -1.5 - \left[ S_{298}^°(\text{RH}) - S_{298}^°(\text{R}^·) \right]$

While rate constants calculated in this way are probably not accurate to better than an order of magnitude, nonetheless they do provide a guide to the reactivities of the polar methoxy and methylamino radicals with polar and non-polar hydrogen substrates.

It will be noted that for both substrates the activation energy for abstraction decreases with increasing strength of the R-H bond formed.
QUANTUM MECHANICAL TUNNELLING.

The Arrhenius parameters derived for hydrogen and deuterium atom abstraction by CF₃⁻ from the methyl positions in CH₃OH/CD₃OH and CH₃NH₂/CD₃NH₂ suggest that tunnelling may be occurring to an appreciable extent. In both cases $E_D - E_H = 1.9$ kcal/mole as against a zero-point energy difference of 1.2 kcal/mole, while the ratio $A_H/A_D$ is less than 1 in both cases. Similar results have been obtained by other workers as shown in Table 54.

TABLE 54.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CD₃OH + CH₃⁻ → CD₂OH + CH₃D</td>
<td>11.9</td>
<td>11.3</td>
<td>1.9</td>
<td>114</td>
</tr>
<tr>
<td>CH₃OH + CH₃⁻ → CH₂OH + CH₄</td>
<td>10.0</td>
<td>11.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-BuD + CD₃⁻ → t-Bu⁻ + CD₄</td>
<td>9.7</td>
<td>11.5</td>
<td>1.6</td>
<td>111</td>
</tr>
<tr>
<td>t-BuH + CD₃⁻ → t-Bu⁻ + CD₃H</td>
<td>8.1</td>
<td>11.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD₃H + CF₃⁻ → CD₂H⁻ + CF₃D</td>
<td>12.7</td>
<td>11.3</td>
<td>2.2</td>
<td>150</td>
</tr>
<tr>
<td>CD₃⁻ + CF₃H</td>
<td>10.5</td>
<td>11.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD₃OH + CF₃⁻ → CD₂OH + CF₃D</td>
<td>6.6</td>
<td>10.2</td>
<td>1.9</td>
<td>This work</td>
</tr>
<tr>
<td>CH₃OH + CF₃⁻ → CH₂OH + CF₃H</td>
<td>4.7</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD₃NH₂ + CF₃⁻ → CD₂NH₂ + CF₃D</td>
<td>6.1</td>
<td>11.0</td>
<td>1.9</td>
<td>This work</td>
</tr>
<tr>
<td>CH₃NH₂ + CF₃⁻ → CH₂NH₂ + CF₃H</td>
<td>4.2</td>
<td>10.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$E$ is in kcal/mole, $A$ in mole⁻¹cm³sec⁻¹.

There is no evidence however, that tunnelling is important in the case of abstraction from the amino group in $(CH₃)₂NH.$
and \((\text{CH}_3)_2\text{ND}\), the difference in activation energies being close to the zero-point energy difference of \(1.3\) kcal/mole. This is in accord with the findings of Gray and his co-workers for systems in which N-H and N-D bonds are broken by methyl radical attack. \((81, 83, 122)\)

**PERFLUOROALDEHYDES AS RADICAL SOURCES**

As was shown in Chapter 7, the reaction

\[
\text{R}_f\text{CHO} + h\nu \rightarrow \text{R}_f\text{H} + \text{CO}
\]

represents an important mode of photodecomposition of perfluoroaldehydes. Reported rate constants for the reaction

\[
\text{R}_f\text{CHO} + \text{R}_f' \rightarrow \text{R}_f\text{H} + \text{R}_f\text{CO}'.
\]

calculated on the assumption that this is the only source of \(\text{R}_f\text{H}\) are therefore likely to be seriously in error. The use of perfluoroaldehydes as radical sources for hydrogen abstraction from other substrates must also lead to high apparent rate constants for the reaction

\[
\text{R}_f' + \text{RH} \rightarrow \text{R}_f\text{H} + \text{R}'.
\]

If the rate of this reaction is sufficiently great, however, the intramolecular contribution to \(\text{RH}\) formation may become unimportant \((124)\). In consequence perfluoroaldehydes are of use for hydrogen abstraction reactions only when the hydrogen atom in the substrate molecule is extremely reactive.

**REACTIONS OF PERFLUOROALKYL RADICALS WITH ALKYL RADICALS**

As mentioned in Chapter 1, cross-combination ratios are normally independent of temperature and close to 2. High, temperature-dependent cross-combination ratios have
been reported for a number of alkyl/perfluoroalkyl radical reactions as shown in Table 55.

**TABLE 55**

<table>
<thead>
<tr>
<th>RADICALS</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃⁺</td>
<td>C₂H₅⁻</td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>i-C₃H₇⁻</td>
</tr>
<tr>
<td>n-C₃H₇⁻</td>
<td>n-C₄H₉⁻</td>
</tr>
<tr>
<td>Δ.</td>
<td>Allyl</td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>CF₃⁻</td>
</tr>
<tr>
<td>CF₃⁻</td>
<td>C₂F₅⁻</td>
</tr>
<tr>
<td>CF₃⁻</td>
<td>n-C₃F₇⁻</td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>n-C₃F₇⁻</td>
</tr>
<tr>
<td>C₂H₅⁻</td>
<td>C₂F₅⁻</td>
</tr>
<tr>
<td>C₂H₅⁻</td>
<td>n-C₃F₇⁻</td>
</tr>
</tbody>
</table>

The value reported for CH₃⁺ and n-C₃F₇⁻ was derived by Pritchard and his co-workers, who photolysed mixtures of acetone and perfluorobutyraldehyde (approx. 3:1), and analysed for C₂H₆, CH₃C₃F₇ and C₆F₁₄. Examination of published data for this system shows that the percentage decomposition of the aldehyde varied systematically from about 7% at low temperatures to around 90% at the top of the temperature range used (300-580°C). In view of the high extent of reaction, it seems possible that at high temperatures secondary reactions such as

\[
CH₃⁺ + CH₃C₃F₇ \rightarrow CH₄ + \cdot CH₂C₃F₇
\]

may have affected the cross-combination ratio. Under these
circumstances it would seem unwise to regard the reported
temperature dependence as conclusively established.

The temperature dependence observed for combination
of C\textsubscript{2}H\textsubscript{5}\textsuperscript{·} with perfluoroalkyl radicals, however, is in accord
with results obtained in the present work for reactions of
CF\textsubscript{3}\textsuperscript{·} with n-C\textsubscript{4}H\textsubscript{9}\textsuperscript{·}, C\textsubscript{6}H\textsubscript{11}\textsuperscript{·} and C\textsubscript{2}H\textsubscript{5}\textsuperscript{·} (Chapters 3 and 7), and
may be explained in terms of the following reactions:-

\[
\begin{align*}
C\textsubscript{2}H\textsubscript{5}\textsuperscript{·} + RF & \xrightarrow{k_d} C\textsubscript{2}H\textsubscript{4} + RFH \\
\downarrow & \\
C\textsubscript{2}H\textsubscript{5}RF & \xleftarrow{k_a} C\textsubscript{2}H\textsubscript{4}RF
\end{align*}
\]

Thus the cross-combination product C\textsubscript{2}H\textsubscript{5}RF is also formed by
an alternative route, leading to a high value of \(\Phi\). Since
both \(k_b\) and \(k_a\) will be temperature dependent, the observed
increase in \(\Phi\) at high temperatures is to be expected. A
similar situation must exist for the combination of alkyl
radicals. However, since \(k_b\) for alkyl radical addition to
olefins is very much lower than for perfluoroalkyl radicals
(61), the effect of this process will normally be negligible.
It seems likely that reported disproportionation/combination
ratios for perfluoroalkyl radicals with ethyl and higher alkyl
radicals will be appreciably lowered by this reaction sequence.

As shown in Chapter 3, reported rate constants for
hydrogen abstraction from alkanes by perfluoroalkyl radicals
are likely to be high, due to the formation of additional
RF\textsubscript{H} by disproportionation. The presence of iodine (atomic
and molecular) in the system appears to inhibit this
reaction by removal of alkyl radicals.
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3. Reactions of Radicals Containing Fluorine. Part 2
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   and Tetramethylsilane by Methyl Radicals.
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    Hydrogen Atom Abstraction from Silane, Trimethylsilane
    and Tetramethylsilane by Trifluoromethyl Radicals.
    E.R. Morris and J.C.J. Thynne
REACTIONS OF METHYL RADICALS WITH FLUOROALDEHYDES

EXPERIMENTAL

...
Reactions of Methyl Radicals with Fluoroaldehydes

By E. R. Morris and J. C. J. Thynne

Chemistry Dept., The University, Edinburgh.

Received 24th April 1967

The reactions of methyl radicals, generated by the thermal decomposition of di-tert butyl peroxide (DTBP), with CF₃CHO, C₂F₅CHO, and C₃F₇CHO have been studied and Arrhenius parameters for the following hydrogen atom abstraction reactions obtained:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log A (mole⁻¹ cm³ sec⁻¹)</th>
<th>E (kcal mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ + DTBP → CH₄ + C₆H₁₇O₂</td>
<td>12.65</td>
<td>11.9</td>
</tr>
<tr>
<td>CH₃ + CF₃CHO → CH₄ + COCF₃</td>
<td>12.10</td>
<td>8.7</td>
</tr>
<tr>
<td>CH₃ + C₂F₅CHO → CH₄ + COC₂F₅</td>
<td>12.93</td>
<td>9.8</td>
</tr>
<tr>
<td>CH₃ + C₃F₇CHO → CH₄ + COC₃F₇</td>
<td>13.19</td>
<td>10.3</td>
</tr>
</tbody>
</table>

The rate of hydrogen atom abstraction from the fluoroaldehydes appears to be independent of the size of the fluoroalkyl group. These results are compared with data for other reactions of the type: CH₃ + HCOX → CH₄ + COX.

Comparison of the relative reactivities of methyl and trifluoromethyl radicals suggests that the nature of the substrate has considerable effect, with hydrocarbons methyl radicals being much less reactive, whereas with polar molecules or molecules containing a weak X—H bond, both radicals react by hydrogen-atom abstraction at similar rates.

Studies of hydrogen-atom abstraction by methyl radicals from molecules of the type HCOX are of interest since the abstraction of the formyl hydrogen atom (reaction (1)),

\[ \text{CH₃ + HCOX → CH₄ + COX} \]  (1)

can be studied conveniently for different side groups and such reactions present the possibility that changes in the velocity constant and the Arrhenius parameters for the abstraction reaction can be correlated with the nature of the substituting group X.

Studies on aldehydes,¹ formates²,³,⁴ and formamides⁵ (i.e., X = R, OR and NR₂) have indicated that although the rate of hydrogen atom abstraction varies markedly between the three families, within a family the rate is independent of the size of the substituting group.

It is desirable to extend these studies to fluoroaldehydes in order to investigate the effect of large, strongly polar groups upon the reactivity of the formyl hydrogen atom and accordingly we have studied the reactions of methyl radicals with trifluorocetaldehyde, pentafluoropropionaldehyde and heptafluoroaldehyde.

EXPERIMENTAL

MATERIALS

Di-tert-butyl peroxide (Koch-Light Co.) was dried and then distilled several times, the middle fractions being collected. It was stored on the vacuum line and was degassed before use.

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TRIFLUOROACETALDEHYDE was prepared from the hydrate (Koch-Light Co.); this was dropped slowly on to a stirred mixture of phosphorous pentoxide and concentrated sulphuric acid at 85-90°C. The gas evolved was collected in two traps, one at -80°C and one at -160°C. After bulb-to-bulb distillation on the vacuum line the aldehyde was stored at -196°C in a blackened bulb. Comparison of the infra-red spectra with the literature spectrum confirmed the identity of the product. PENTAFLUOROPROPIONALDEHYDE and HEPTAFLUOROBUTYRALDEHYDE were similarly prepared from their hydrates (Eastman Kodak).

APPARATUS AND PROCEDURE

The reaction cell was a spherical Pyrex vessel (184 cm³) housed in an electric furnace, the temperature of which was controlled by a Bikini-Fenwall relay unit to ±0·2°C. The cell was connected by a short-side-arm to a conventional high-vacuum apparatus comprising cold traps, gas burette and Macleod gauge. Mixtures of the aldehyde and peroxide were made up in a large bulb, (using a dibutyl phthalate manometer for pressure measurements), before expansion into the cell. After reaction the contents of the reaction cell were expanded into a liquid-nitrogen-cooled trap. The non-condensable fraction was collected and measured in the gas burette before being analyzed mass-spectrometrically by an AEI Ltd. MS 10 mass spectrometer. This fraction contained methane and carbon monoxide. A further fraction volatile at -160°C was collected, measured and analyzed mass spectrometrically. This fraction comprised mainly ethane (plus a little carbon dioxide impurity from the aldehyde which could not be removed after prolonged pumping). With trifluoroacetaldehyde, for decomposition was greater than about 5 %, other peaks were observed in the mass spectrum of the -160°C fraction. These correspond to m/e values of 31, 45, 51, 69 and 119 and presumably arise from products such as CF₃H, CF₃CH₃ and C₂F₆. In order to avoid substantial corrections for these products the aldehyde was decomposed to only a small extent (<3 %). No such contamination of the -160°C fraction was observed with the other aldehydes.

RESULTS

When methyl radicals are generated in the presence of di-tert-butyl peroxide (DTBP) and the fluoroaldehydes, methane is formed by hydrogen atom abstraction from both molecules. In order to correct for the methane formed from DTBP a study of this reaction was made.

HYDROGEN-ATOM ABSTRACTION FROM DTBP BY Methyl RADICALS

DTBP was thermally decomposed over the temperature range 127-171°C. Methane and ethane are formed by the following reactions:

\[
\begin{align*}
\text{CH}_3 + \text{DTBP} & \rightarrow \text{CH}_4 + \text{C}_8\text{H}_7\text{O}_2 \\
2\text{CH}_3 & \rightarrow \text{C}_2\text{H}_6
\end{align*}
\]

(2)

(3)

Under steady-state conditions the following rate relation may be deduced, where \( R_x \) is the rate of formation of \( X \) and (DTBP) is the mean concentration of the peroxide:

\[
R_{\text{CH}_4} = \frac{k_2^{+}}{k_1} (\text{DTBP}) = k_2/k_1.
\]

Using the value \(^7\) of 10\(^{13.34}\) (mole\(^{-1}\) cm\(^3\) sec\(^{-1}\)) for the velocity constant of combination of methyl radicals, our data, when analyzed by the method of least-mean-squares, are expressed by the equation:

\[
\log k_2 (\text{mole}^{-1}\text{ cm}^3\text{ sec}^{-1}) = (12.65 \pm 0.18) - (11900 \pm 300)/2.303RT
\]

The error limits quoted in this paper are the standard deviations. These Arrhenius parameters are in reasonable agreement with values of \(^8\) 12·4 for log \( A_2 \) and 11·7 and 14·5 ± 2·5 kcal mole\(^{-1}\) for \( E_2 \).
Table 1.—Hydrogen-atom abstraction from fluoroaldehydes \([\text{HCOX}]\) by methyl radicals.

<table>
<thead>
<tr>
<th>temp (°K)</th>
<th>time (sec)</th>
<th>([\text{HCOX}]) (10^6 mole cm(^{-3}))</th>
<th>([\text{DTBP}]) (10^12 mole cm(^{-3}) sec(^{-1}))</th>
<th>(R_{\text{CH}<em>4(\text{abs})}/R</em>{\text{C}_2\text{H}_6[\text{HCOX}]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRIFLUOROACETALDEHYDE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>401.1</td>
<td>2500</td>
<td>0.59</td>
<td>0.28</td>
<td>2.23</td>
</tr>
<tr>
<td>401.5</td>
<td>480</td>
<td>0.49</td>
<td>0.24</td>
<td>2.45</td>
</tr>
<tr>
<td>405.2</td>
<td>750</td>
<td>0.53</td>
<td>0.40</td>
<td>5.02</td>
</tr>
<tr>
<td>409.7</td>
<td>600</td>
<td>0.69</td>
<td>0.35</td>
<td>7.86</td>
</tr>
<tr>
<td>415.1</td>
<td>1200</td>
<td>0.59</td>
<td>0.27</td>
<td>9.50</td>
</tr>
<tr>
<td>421.4</td>
<td>240</td>
<td>0.59</td>
<td>0.24</td>
<td>21.6</td>
</tr>
<tr>
<td>421.4</td>
<td>300</td>
<td>0.64</td>
<td>0.36</td>
<td>21.6</td>
</tr>
<tr>
<td>421.4</td>
<td>200</td>
<td>0.57</td>
<td>0.36</td>
<td>21.2</td>
</tr>
<tr>
<td>429.2</td>
<td>180</td>
<td>0.56</td>
<td>0.28</td>
<td>35.5</td>
</tr>
<tr>
<td>429.2</td>
<td>200</td>
<td>0.58</td>
<td>0.27</td>
<td>41.0</td>
</tr>
<tr>
<td>435.6</td>
<td>200</td>
<td>0.43</td>
<td>0.16</td>
<td>32.1</td>
</tr>
<tr>
<td>436.2</td>
<td>120</td>
<td>0.68</td>
<td>0.30</td>
<td>94.3</td>
</tr>
<tr>
<td>440.9</td>
<td>100</td>
<td>0.61</td>
<td>0.29</td>
<td>110.8</td>
</tr>
<tr>
<td>443.8</td>
<td>120</td>
<td>0.65</td>
<td>0.30</td>
<td>142.9</td>
</tr>
<tr>
<td>444.2</td>
<td>120</td>
<td>0.53</td>
<td>0.24</td>
<td>95.0</td>
</tr>
<tr>
<td>444.8</td>
<td>150</td>
<td>0.53</td>
<td>0.22</td>
<td>101.0</td>
</tr>
</tbody>
</table>

PENTAFLUOROPROPIONALDEHYDE

<table>
<thead>
<tr>
<th>temp (°K)</th>
<th>time (sec)</th>
<th>([\text{HCOX}]) (10^6 mole cm(^{-3}))</th>
<th>([\text{DTBP}]) (10^12 mole cm(^{-3}) sec(^{-1}))</th>
<th>(R_{\text{CH}<em>4(\text{abs})}/R</em>{\text{C}_2\text{H}_6[\text{HCOX}]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>398.2</td>
<td>3600</td>
<td>0.22</td>
<td>0.12</td>
<td>0.91</td>
</tr>
<tr>
<td>398.2</td>
<td>1800</td>
<td>0.23</td>
<td>0.15</td>
<td>1.42</td>
</tr>
<tr>
<td>403.0</td>
<td>600</td>
<td>0.26</td>
<td>0.17</td>
<td>2.48</td>
</tr>
<tr>
<td>403.2</td>
<td>540</td>
<td>0.26</td>
<td>0.17</td>
<td>2.61</td>
</tr>
<tr>
<td>408.2</td>
<td>1200</td>
<td>0.19</td>
<td>0.13</td>
<td>2.33</td>
</tr>
<tr>
<td>408.2</td>
<td>900</td>
<td>0.25</td>
<td>0.19</td>
<td>4.49</td>
</tr>
<tr>
<td>413.0</td>
<td>480</td>
<td>0.23</td>
<td>0.11</td>
<td>4.74</td>
</tr>
<tr>
<td>413.2</td>
<td>480</td>
<td>0.30</td>
<td>0.16</td>
<td>6.33</td>
</tr>
<tr>
<td>418.4</td>
<td>420</td>
<td>0.30</td>
<td>0.19</td>
<td>11.4</td>
</tr>
<tr>
<td>423.2</td>
<td>480</td>
<td>0.26</td>
<td>0.16</td>
<td>14.2</td>
</tr>
<tr>
<td>428.2</td>
<td>420</td>
<td>0.22</td>
<td>0.15</td>
<td>15.6</td>
</tr>
<tr>
<td>433.6</td>
<td>480</td>
<td>0.19</td>
<td>0.10</td>
<td>16.6</td>
</tr>
<tr>
<td>438.2</td>
<td>240</td>
<td>0.18</td>
<td>0.08(_a)</td>
<td>18.5</td>
</tr>
<tr>
<td>438.2</td>
<td>300</td>
<td>0.17</td>
<td>0.10</td>
<td>22.0</td>
</tr>
</tbody>
</table>

HEPTAFLUOROBUTYRALDEHYDE

<table>
<thead>
<tr>
<th>temp (°K)</th>
<th>time (sec)</th>
<th>([\text{HCOX}]) (10^6 mole cm(^{-3}))</th>
<th>([\text{DTBP}]) (10^12 mole cm(^{-3}) sec(^{-1}))</th>
<th>(R_{\text{CH}<em>4(\text{abs})}/R</em>{\text{C}_2\text{H}_6[\text{HCOX}]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>398.2</td>
<td>3600</td>
<td>0.31</td>
<td>0.14</td>
<td>1.15</td>
</tr>
<tr>
<td>398.4</td>
<td>1800</td>
<td>0.33</td>
<td>0.14</td>
<td>1.26</td>
</tr>
<tr>
<td>403.2</td>
<td>1620</td>
<td>0.26</td>
<td>0.17</td>
<td>1.51</td>
</tr>
<tr>
<td>403.2</td>
<td>1200</td>
<td>0.28</td>
<td>0.17</td>
<td>2.28</td>
</tr>
<tr>
<td>408.4</td>
<td>1200</td>
<td>0.25</td>
<td>0.12</td>
<td>2.48</td>
</tr>
<tr>
<td>408.2</td>
<td>1800</td>
<td>0.32</td>
<td>0.15</td>
<td>3.33</td>
</tr>
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<td>0.14</td>
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<td>6.88</td>
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<td>0.15</td>
<td>16.7</td>
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<tr>
<td>433.2</td>
<td>360</td>
<td>0.18</td>
<td>0.10</td>
<td>16.5</td>
</tr>
<tr>
<td>438.4</td>
<td>300</td>
<td>0.19</td>
<td>0.09</td>
<td>24.2</td>
</tr>
</tbody>
</table>
METHANE AND ETHANE FORMATION DURING THERMAL DECOMPOSITION OF DTBP IN PRESENCE OF R₂CHO.

When DTBP is thermally decomposed in the presence of the fluoroaldehydes the following reactions need to be added to the reaction scheme above to account for the methane formation:

\[
\begin{align*}
\text{CH}_3 + \text{CF}_3\text{CHO} & \rightarrow \text{CH}_4 + \text{CF}_3\text{CO} \\
\text{CH}_3 + \text{C}_2\text{F}_5\text{CHO} & \rightarrow \text{CH}_4 + \text{C}_2\text{F}_5\text{CO} \\
\text{CH}_3 + \text{C}_3\text{F}_7\text{CHO} & \rightarrow \text{CH}_4 + \text{C}_3\text{F}_7\text{CO}
\end{align*}
\]

If \( R_{\text{CH}_4} \) (4) is the steady rate of production of methane by reaction (4), obtained by subtracting from the total methane that part which comes from reaction (2), then the following rate relation applies:

\[
R_{\text{CH}_4(4)}/R_{\text{CH}_4(\text{ald})} = k_4/k_2
\]

where \( \text{(ald)} \) refers to the mean concentration of \( \text{CF}_3\text{CHO} \). Similar rate relations can be obtained for the other aldehydes.

Our results for the three aldehydes are given in table 1. These data when treated by the method of least squares are represented by the following equations:

\[
\begin{align*}
\log k_4 \text{ (mole}^{-1}\text{ cm}^3\text{ sec}^{-1} & = (12.10 \pm 0.16) - (8700 \pm 300)/2.303RT, \\
\log k_5 \text{ (mole}^{-1}\text{ cm}^3\text{ sec}^{-1} & = (12.93 \pm 0.21) - (9800 \pm 300)/2.303RT, \\
\log k_6 \text{ (mole}^{-1}\text{ cm}^3\text{ sec}^{-1} & = (13.19 \pm 0.18) - (10300 \pm 400)/2.303RT.
\end{align*}
\]

There are no other Arrhenius parameters reported for any of these reactions. At 164°C the rate constants \( k_4, k_5 \) and \( k_6 \) have values of \( 10^7.8, 10^8.0 \) and \( 10^8.0 \) respectively (in mole\(^{-1}\) cm\(^3\) sec\(^{-1}\)) and so within experimental error are identical.

DISCUSSION

HYDROGEN ATOM ABSTRACTION FROM R₂CHO

The similarity of the rate constants for hydrogen atom abstraction from the three aldehydes indicates that all of the formyl hydrogen atoms are similarly reactive and that the size of the substituting group does not influence the reactivity of the formyl hydrogen. This is in general accord with the results reported for the aldehydes,\(^1\) formates \(^2\text{-}^4\) and formamides.\(^5\)

In table 2 we have compared Arrhenius parameter and rate constant data for hydrogen atom abstraction by methyl radicals from substrates of the type HCOX.
Although comparison of the molecules $X = R$, NR$_2$ and OR would suggest that the reaction rate decreased as the electronegativity of the side group increased, where $X = R_1$ the trend is not sustained and the reactivity of the fluoroaldehydes is only slightly less than that of the aldehydes. This suggests that the effect of fluorine atoms being substituted for hydrogen is to cause only slight deactivation of the hydrogen atom on the adjacent carbon atom.

The activation energies required for abstraction are appreciably larger for the fluoroaldehydes than for any of the other comparable substrates so that it might be predicted that $D(H—COR_f) > D(H—COX)$. Also, the pre-exponential factors are about 10 times larger than usually observed for reactions of this nature. For methyl radicals reacting with a variety of aldehydes the pre-exponential factors varied from $10^{11.9}$ to $10^{13.1}$, values appreciably larger than those usually found. Since “normal” values were reported for the formates and formamides it suggests that these high values are a common property of the aldehydes.

The activation energies required for hydrogen-atom abstraction increase steadily as the side group gets larger. The increase is outside the experimental error and might indicate that the H—COR bond was increasing in strength although the similarity in rate constants is evidence against this. Birrell and Trotman-Dickenson observed that branching in the alkyl group was accompanied by a small increase in the Arrhenius parameters for hydrogen atom abstraction.

**COMPARISON OF Reactivity OF CH$_3$ AND CF$_3$ RADICALS**

Pritchard et al. have suggested, on the basis of the hydrogen-atom abstraction reactions of methyl and trifluoromethyl radicals with hydrocarbon substrates, that CF$_3$ radicals are considerably more reactive and that this difference in reactivity stems from activation energy differences of 3-4 kcal mole$^{-1}$ between the two radicals. In table 3 we show data for attack by CH$_3$ and CF$_3$ radicals on molecules which lose hydrogen atoms readily to methyl radicals. For some of these systems various values have been reported for the activation energies. We have taken values near the average of these values or for H$_2$S that we considered to be the “best” value.

For molecules such as H$_2$S and CF$_3$CHO, hydrogen-atom abstraction by CF$_3$ radicals occurs at a similar (possibly slightly slower) rate as that with methyl radicals, and there is little difference in either the activation energies or the $A$-factors. For these molecules it is likely that the strength of the bond being broken is about 90-95 kcal mole$^{-1}$, i.e., much weaker than the bond being formed, whereas for the hydrocarbons there is much less difference between the bonds broken and formed. These results

<table>
<thead>
<tr>
<th>$E_{CH_3}$</th>
<th>$E_{CF_3}$</th>
<th>$\Delta E$</th>
<th>$\log (A_{CH_3}/A_{CF_3})$</th>
<th>$k_{CF_3}/k_{CH_3}(164°C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.7</td>
<td>10.3</td>
<td>4.4</td>
<td>0.13</td>
<td>118</td>
</tr>
<tr>
<td>11.8</td>
<td>7.5</td>
<td>4.3</td>
<td>0.53</td>
<td>42</td>
</tr>
<tr>
<td>9.6</td>
<td>5.3</td>
<td>4.3</td>
<td>0.44</td>
<td>50</td>
</tr>
<tr>
<td>2.6</td>
<td>3.9</td>
<td>1.3</td>
<td>-0.25</td>
<td>0.4</td>
</tr>
<tr>
<td>8.7</td>
<td>8.2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>ref. 15, 14</td>
<td>15, 14</td>
<td>15, 16</td>
<td>17, 18, 12, this work</td>
<td></td>
</tr>
</tbody>
</table>

In table 3 we have also included data for attack by CH$_3$ and CF$_3$ radicals on molecules which lose hydrogen atoms readily to methyl radicals. For some of these systems various values have been reported for the activation energies. We have taken values near the average of these values or for H$_2$S that we considered to be the “best” value.
might be explained in terms that the C—H bond strength has declined in strength to the stage where there is no difference in activation energy required for the two radicals. It is possible, however, that it is the polarity of the molecules which is the important factor and for molecules such as H₂S, repulsion forces between the radical and the molecule are significant and the activation energy is increased compared to the values observed with non-polar molecules.

Pritchard et al.¹¹ have considered that the activation energy of 8.2 kcal mole⁻¹ reported by Dodd and Smith¹² for the reaction:

\[ \text{CF}_3\text{HOCOCF}_3 \rightarrow \text{CF}_3\text{H} + \text{COCF}_3 \]  

(7) to be improbably high, because an activation energy difference of ca. 3-4 kcal mole⁻¹ for methyl and trifluoromethyl radicals attacking the same molecule would suggest an activation energy of ca. 12 kcal mole⁻¹ for reaction (4). Comparison of Dodd and Smith’s value for reaction (7) with our measured value for \( E^* \) indicates that their value is probably accurate and is compatible with other hydrogen atom abstraction data from polar molecules by trifluoromethyl radicals.

We thank the Laporte Chemical Co., for their support of this work, Dr. J. H. Knox of this department for many helpful discussions, and Mr. N. C. Beaton for performing some of the experiments.

Reactions of Radicals Containing Fluorine

Part 1.—Hydrogen and Deuterium Atom Abstraction from Trideuteromethanol by Trifluoromethyl Radicals

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The reactions of trifluoromethyl radicals with methanol and trideuteromethanol have been studied in the temperature range 84-162°C in order to determine the rate at which hydrogen and deuterium atom abstraction occurs. Over this temperature range, abstraction from the hydroxyl group is slightly favoured over abstraction from the methyl group. Substitution of deuterium for hydrogen alters the positional reactivity by an amount in accord with the zero-point energy difference.

Arrhenius parameters (based upon a value of 10^{13.34} \text{mole}^{-1} \text{cm}^3 \text{sec}^{-1} of the rate constant of combination of trifluoromethyl radicals) have been measured for the reactions:

\[
\begin{align*}
\text{CF}_3 + \cdot \text{C}_2 \text{H}_10 & \rightarrow \text{CF}_3 \text{H} + \text{C}_2 \text{H}_6 & 11.3 & 5.7 \\
\text{CF}_3 + \text{CH}_3 \text{OH} & \rightarrow \text{CF}_3 \text{H} + (\text{COH}_3) & 9.9 & 3.7 \\
\text{CF}_3 + \text{CD}_3 \text{OH} & \rightarrow \text{CF}_3 \text{H} + \text{CD}_3 \text{O} & 9.5 & 3.2 \\
\text{CF}_3 + \text{CD}_3 \text{OH} & \rightarrow \text{CF}_3 \text{D} + \text{CD}_2 \text{OH} & 10.2 & 6.6 \\
\text{CF}_3 + \text{CH}_3 \text{OH} & \rightarrow \text{CF}_3 \text{H} + \text{CH}_2 \text{OH} & 10.0 & 4.7
\end{align*}
\]

and have been calculated for

\[
\begin{align*}
\text{CH}_3 \text{O} + \text{CF}_3 \text{H} & \rightarrow \text{CH}_3 \text{OH} + \text{CF}_3 & 9.5 & 7.7
\end{align*}
\]

(units of \(A \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}\) and \(E \text{ kcal mole}^{-1}\)).

The reactions of the lower fluoroalkyl radicals with hydrocarbons have received much attention \(^1\) and it has been suggested \(^2\) that, for hydrogen atom abstraction reactions, the activation energies required are ca. 3 kcal mole\(^{-1}\) lower and the reaction rates much higher for the reactions involving fluoroalkyl radicals than for the alkyl radicals. There are few data \(^3-5\) reported for the hydrogen atom abstraction reactions of fluoroalkyl radicals with polar molecules; however, these suggest that there are much smaller differences between both the activation energies and the reaction rate constants for such reactions and the values observed for alkyl radicals. It is not clear to what extents the polarity of the substrate molecule or the strength of the bond being broken determine the reaction rates in such cases. A molecule such as methanol should provide information in this respect, and by using CD\(_3\)OH the relative reactivities of the hydrogen atoms attached to the carbon and oxygen atoms may be evaluated. Carlton \textit{et al.}\(^6\) have reported data for this reaction; however, our preliminary experiments showed completely different rates of attack on the CD\(_3\)OH from their results and accordingly we carried out an investigation of the reaction of trifluoromethyl radicals with methanol and trideuteromethanol.

**EXPERIMENTAL**

Hexafluoroacetone (HFA) and hexafluoroazomethane (HFAM) are the two sources normally used to generate trifluoromethyl radicals. However, because of the reactivity of the carbonyl group in HFA with molecules such as methanol, methyl mercaptan and
methylamine, it cannot be used as a radical source with such substrates. HFAM is a photochemical source of trifluoromethyl radicals but suffers from the disadvantage that these radicals react extremely readily by the addition to the parent molecule.

Trifluoromethyl iodide (TFMI) is a good photolytic source of CF₃ radicals. It does not react with methanol and accordingly we have used this as our radical source.

**MATERIALS**

TRIFLUOROMETHYL IODIDE (Pierce Chemical Co.) contained small amounts of fluoroform, hexafluoroethane and carbon dioxide. These were removed by low-temperature distillation at -130°C in a vacuum line.

HEXAFLUOROACETONE (Dupont Co.) contained fluoroform, hexafluoroethane, tetrafluoroethylene and carbon dioxide. These were removed as stated above.

TRIDEUTEROMETHANOL (Merck Sharp and Dohme,) METHANOL and n-BUTANE were thoroughly degassed and stored on the vacuum line.

**PROCEDURE**

The reaction cell was a quartz cylinder (volume 218 cm³) which was housed in a heavy aluminium block furnace fitted with quartz side windows. A modified Bikini-Fenwal relay unit controlled the furnace temperature to better than ±0.2°C. The reaction cell was fitted with a Teflon stopcock and metal valves were used in the analytical system. The light source was an Hanovia 220 W mercury lamp and a parallel beam from the full arc was used.

Reaction mixtures of the radical source and the substrate were made up by making use of a butyl phthalate manometer. Within our experimental error no changes in pressures were observed in mixing TFMI with methanol or n-butane or HFA with n-butane. On mixing HFA and methanol a considerable pressure decrease was observed and a white crystalline solid was formed.

After reaction the contents of the cell were expanded into the analytical train and collected in a liquid-nitrogen trap. After the removal of carbon monoxide (when HFA was used) by pumping, the contents of the trap were transferred quantitatively by a Toepler pump to the injection system of the gas chromatography apparatus. The analysis of C₂F₆ and CF₃H was performed on a 3 m column of silica gel at 50°C using hydrogen as a carrier gas and a Gow-Mac thermistor detector. In experiments involving CD₂OH, CF₃H and CF₃D were eluted from the column together and were trapped in a U-tube at -196°C. They were then analyzed mass-spectrometrically using an AEI Ltd. MS 10 mass spectrometer. The sensitivities of CF₃H and CF₃D were assumed to be the same and the peaks at m/e equal to 51 and 52 were used in the analysis, a correction being applied to the 52 peak for the contribution from 1²CF₃H⁺.

**RESULTS**

As a check on our experimental and analytical technique we studied the reaction of n-butane with CF₃ radicals using the photolyses of HFA and TFMI to generate the radicals. This reaction was chosen since it has been studied by other workers.

HYDROGEN ATOM ABSTRACTION FROM n-BUTANE USING HFA.—When CF₃ radicals are generated in the presence of n-butane, fluoroform and hexafluoroethane are formed by the following reactions:

\[
\begin{align*}
1 & \quad CF₃ + C₄H₁₀ \rightarrow CF₃H + C₄H₉ \\
2 & \quad 2CF₃ \rightarrow C₂F₆
\end{align*}
\]

Our data, given in table 1, are represented by the equation.

\[
\log k₁(mole^{-1} \text{ cm}³ \text{ sec}^{-1}) = (11.77 \pm 0.24) - (6190 \pm 430)/2.303RT,
\]
where the error limits are the standard deviations of a least-mean-squares computer treatment and the rate constant of combination of trifluoromethyl radicals is assumed^7 to be \(10^{13.34}\) (mole\(^{-1}\) cm\(^3\) sec\(^{-1}\)). Other values reported,^8,9 for the Arrhenius parameters of reaction (1) are \(11\cdot15\) (mole\(^{-1}\) cm\(^3\) sec\(^{-1}\)) and 5.1 (kcal mole\(^{-1}\)) and 11.46 and 5.3.

Table 1.—Hydrogen atom abstraction from \(\beta\)-butane by trifluoromethyl radicals (using HFA).

<table>
<thead>
<tr>
<th>(T^\circ K)</th>
<th>(t) (sec)</th>
<th>(C_4H_{10})</th>
<th>HFA</th>
<th>(C_2F_6)</th>
<th>(k_1/k_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>357.1</td>
<td>45</td>
<td>0.391</td>
<td>1.44</td>
<td>58.7</td>
<td>50.5</td>
</tr>
<tr>
<td>357.1</td>
<td>45</td>
<td>0.586</td>
<td>1.66</td>
<td>65.9</td>
<td>29.1</td>
</tr>
<tr>
<td>370.2</td>
<td>45</td>
<td>1.65</td>
<td>0.747</td>
<td>86.3</td>
<td>4.95</td>
</tr>
<tr>
<td>370.2</td>
<td>180</td>
<td>1.62</td>
<td>0.735</td>
<td>82.1</td>
<td>4.83</td>
</tr>
<tr>
<td>370.3</td>
<td>90</td>
<td>0.423</td>
<td>1.04</td>
<td>100.1</td>
<td>29.8</td>
</tr>
<tr>
<td>370.5</td>
<td>90</td>
<td>0.724</td>
<td>0.766</td>
<td>99.2</td>
<td>21.2</td>
</tr>
<tr>
<td>384.5</td>
<td>60</td>
<td>0.415</td>
<td>1.89</td>
<td>117.1</td>
<td>50.1</td>
</tr>
<tr>
<td>400.0</td>
<td>60</td>
<td>0.551</td>
<td>1.56</td>
<td>177.9</td>
<td>39.6</td>
</tr>
<tr>
<td>400.0</td>
<td>45</td>
<td>0.276</td>
<td>1.26</td>
<td>120.4</td>
<td>67.4</td>
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<tr>
<td>416.6</td>
<td>45</td>
<td>0.980</td>
<td>0.977</td>
<td>226.6</td>
<td>10.1</td>
</tr>
<tr>
<td>416.6</td>
<td>90</td>
<td>1.27</td>
<td>0.57</td>
<td>175.8</td>
<td>5.10</td>
</tr>
<tr>
<td>434.6</td>
<td>45</td>
<td>0.371</td>
<td>1.69</td>
<td>315.0</td>
<td>63.8</td>
</tr>
<tr>
<td>434.8</td>
<td>45</td>
<td>0.318</td>
<td>1.17</td>
<td>262.5</td>
<td>71.0</td>
</tr>
<tr>
<td>434.9</td>
<td>60</td>
<td>0.450</td>
<td>1.27</td>
<td>279.1</td>
<td>39.7</td>
</tr>
</tbody>
</table>

\(C_4H_{10}\) and HFA in \(10^{-6}\) mole cm\(^{-3}\); \(C_2F_6\) in \(10^{-12}\) mole cm\(^{-3}\) sec\(^{-1}\).

Using TFMI.—When TFMI was used as the radical source over the same temperature and concentration ranges, values for \(k_1\) were obtained which were consistently lower than the values obtained using the ketone as the radical source. Our data given in table 2 are expressed by

\[
\log k_1 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (11.31 \pm 0.16) - (5740 \pm 280)/2.303RT.
\]

Table 2.—Hydrogen atom abstraction from \(\beta\)-butane by trifluoromethyl radicals (using TFMI).

<table>
<thead>
<tr>
<th>(T^\circ K)</th>
<th>(t) (sec)</th>
<th>(C_4H_{10})</th>
<th>TFMI</th>
<th>(C_2F_6)</th>
<th>(k_1/k_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>357.1</td>
<td>450</td>
<td>0.419</td>
<td>1.58</td>
<td>7.78</td>
<td>1.27</td>
</tr>
<tr>
<td>357.2</td>
<td>900</td>
<td>0.479</td>
<td>1.71</td>
<td>8.56</td>
<td>1.05</td>
</tr>
<tr>
<td>370.3</td>
<td>450</td>
<td>0.162</td>
<td>1.99</td>
<td>5.80</td>
<td>4.31</td>
</tr>
<tr>
<td>370.3</td>
<td>450</td>
<td>0.232</td>
<td>1.48</td>
<td>15.1</td>
<td>1.55</td>
</tr>
<tr>
<td>370.5</td>
<td>450</td>
<td>0.841</td>
<td>0.816</td>
<td>17.0</td>
<td>1.22</td>
</tr>
<tr>
<td>384.6</td>
<td>450</td>
<td>0.439</td>
<td>1.65</td>
<td>12.5</td>
<td>1.22</td>
</tr>
<tr>
<td>400.2</td>
<td>450</td>
<td>0.463</td>
<td>1.65</td>
<td>14.7</td>
<td>1.07</td>
</tr>
<tr>
<td>416.4</td>
<td>450</td>
<td>0.145</td>
<td>1.79</td>
<td>11.2</td>
<td>3.56</td>
</tr>
<tr>
<td>416.6</td>
<td>180</td>
<td>0.775</td>
<td>0.752</td>
<td>41.9</td>
<td>1.75</td>
</tr>
<tr>
<td>416.7</td>
<td>200</td>
<td>0.628</td>
<td>1.29</td>
<td>1.75</td>
<td>41.1</td>
</tr>
<tr>
<td>434.8</td>
<td>300</td>
<td>0.410</td>
<td>1.54</td>
<td>30.3</td>
<td>1.41</td>
</tr>
<tr>
<td>434.9</td>
<td>450</td>
<td>0.315</td>
<td>1.13</td>
<td>18.4</td>
<td>0.804</td>
</tr>
</tbody>
</table>

\(C_4H_{10}\) and TFMI in \(10^{-6}\) mole cm\(^{-3}\); \(C_2F_6\) in \(10^{-12}\) mole cm\(^{-3}\) sec\(^{-1}\).

Although our two equations give values for \(k_1\) which agree within the standard deviation limits, comparison of the final columns of tables 1 and 2 shows the rate constant ratio \((k_1/k_2)\) to be more nearly constant over a wide concentration range for TFMI + \(C_4H_{10}\) mixtures than for HFA + \(C_4H_{10}\) mixtures. This suggests an
additional reaction leading to the formation of CF₃H in the latter system. Examination of the reaction products for this system showed that appreciable yields of butene-1 and cis- and trans-butene 2 were formed, presumably by the reactions:

\[
\begin{align*}
3 & \text{CF}_3 + \text{CH}_2\text{CHCH}_2\text{CH}_3 \rightarrow \text{CF}_3\text{H} + \text{CH}_3\text{CH} = \text{CHCH}_3 \\
4 & \text{CF}_3 + \text{CH}_2\text{CHCH}_2\text{CH}_3 \rightarrow \text{CF}_2\text{H} + \text{CH}_2 = \text{CHCH}_2\text{CH}_3 \\
5 & \text{CF}_3 + \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CF}_3\text{H} + \text{CH}_2 = \text{CH}_2 + \text{CHCH}_2\text{CH}_3.
\end{align*}
\]

Participation of these reactions would lead to an apparent excess of CF₃H formation by reaction (1).

When TFMI was the radical source butene formation was inhibited. Since iodine atoms are generated in the primary photolytic act they are present (with molecular iodine) in high concentrations in the reaction system and can readily react with the hydrocarbon radicals produced in the initial abstraction reaction (1), i.e.

\[
\text{I} + \text{C}_4\text{H}_9 \rightarrow \text{C}_4\text{H}_9\text{I}.
\]

The occurrence of such a reaction would prevent CF₃H formation by reactions (3)-(5). We consider it unlikely that there is any contribution to CF₃H formation by reactions (7) and (8) because of the inhibition of butene formation when TFMI + C₄H₁₀ mixtures are photolyzed:

\[
\begin{align*}
7 & \text{I} + \text{C}_4\text{H}_9 \rightarrow \text{HI} + \text{C}_4\text{H}_8 \\
8 & \text{CF}_3 + \text{HI} \rightarrow \text{CF}_3\text{H} + \text{I}.
\end{align*}
\]

The A-factor obtained using HFA is higher than that obtained using TFMI. Benson has suggested that the occurrence of secondary reactions between the generating radical and the product radical would lead to a low A-factor. It appears from our data that the A-factor is not noticeably affected by such a reaction. Unpublished results obtained in this laboratory using cyclohexane show the same behaviour.

CF₃H, CF₃D AND C₂F₆ FORMATION IN PRESENCE OF CH₃OH

When CF₃ radicals (from TFMI) are produced in the presence of trideuteromethanol the products observed and analyzed quantitatively were CF₃H, CF₃D and C₂F₆. Small quantities of CD₄ and CD₃H were also observed among the permanent gas fraction. Their formation is accounted for by the following reaction scheme:

\[
\text{CF}_3 + \text{CD}_3\text{OH} \rightarrow \text{CF}_3\text{H} + \text{CD}_3\text{O}
\]

\[
\rightarrow \text{CF}_3\text{D} + \text{CD}_2\text{OH}
\]

The following steady-state relationships apply:

\[
R_{\text{CF}_3\text{H}}/R_{\text{CD}_3\text{OH}} = k_9/k_1 \quad \text{and} \quad R_{\text{CF}_3\text{D}}/R_{\text{CD}_3\text{OH}} = k_{10}/k_2,
\]

where [CD₃OH] denotes the concentration of trideuteromethanol. Our results are shown in table 3 and, when treated by the method of least-mean-squares, are represented by the equations (using \(k_2 = 10^{+13-14}\)):

\[
\log k_9 \ (\text{mole}^{-1} \text{cm}^3 \text{sec}^{-1}) = (9.48 \pm 0.35) - (3240 \pm 630)/2.303RT,
\]

and

\[
\log k_{10} \ (\text{mole}^{-1} \text{cm}^3 \text{sec}^{-1}) = (10.20 \pm 0.23) - (6610 \pm 630)/2.303RT.
\]
Trifluoromethyl radical reactions

Table 3.—Hydrogen and deuterium atom abstraction from \( \text{CD}_3\text{OH} \) by trifluoromethyl radicals

<table>
<thead>
<tr>
<th>T°K</th>
<th>( t ) (sec)</th>
<th>( \text{CD}_3\text{OH} )</th>
<th>TFMI</th>
<th>( \text{CF}_3\text{H} )</th>
<th>( \text{CF}_3\text{D} )</th>
<th>( \text{C}_2\text{F}_6 )</th>
<th>( A )</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>357-1</td>
<td>1200</td>
<td>0.395</td>
<td>1.59</td>
<td>1.72</td>
<td>0.077</td>
<td>0.877</td>
<td>4.6</td>
<td>0.210</td>
</tr>
<tr>
<td>357-1</td>
<td>1500</td>
<td>0.291</td>
<td>1.57</td>
<td>1.69</td>
<td>0.076</td>
<td>0.711</td>
<td>6.9</td>
<td>0.311</td>
</tr>
<tr>
<td>357-1</td>
<td>1800</td>
<td>0.249</td>
<td>1.76</td>
<td>1.62</td>
<td>0.073</td>
<td>0.650</td>
<td>8.1</td>
<td>0.366</td>
</tr>
<tr>
<td>370-2</td>
<td>1200</td>
<td>0.182</td>
<td>1.29</td>
<td>1.35</td>
<td>0.071</td>
<td>0.730</td>
<td>8.6</td>
<td>0.458</td>
</tr>
<tr>
<td>384-5</td>
<td>1800</td>
<td>0.278</td>
<td>1.50</td>
<td>1.72</td>
<td>0.109</td>
<td>0.617</td>
<td>7.9</td>
<td>0.497</td>
</tr>
<tr>
<td>384-6</td>
<td>2400</td>
<td>0.210</td>
<td>1.45</td>
<td>1.73</td>
<td>0.019</td>
<td>0.458</td>
<td>12.1</td>
<td>0.769</td>
</tr>
<tr>
<td>400-0</td>
<td>1800</td>
<td>0.202</td>
<td>1.43</td>
<td>1.67</td>
<td>0.125</td>
<td>0.638</td>
<td>10.3</td>
<td>0.772</td>
</tr>
<tr>
<td>400-0</td>
<td>2500</td>
<td>0.335</td>
<td>1.35</td>
<td>2.24</td>
<td>0.168</td>
<td>0.350</td>
<td>11.2</td>
<td>0.838</td>
</tr>
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<td>416-6</td>
<td>1800</td>
<td>0.348</td>
<td>0.788</td>
<td>2.25</td>
<td>0.199</td>
<td>0.357</td>
<td>10.8</td>
<td>0.959</td>
</tr>
<tr>
<td>416-8</td>
<td>1800</td>
<td>0.237</td>
<td>0.953</td>
<td>2.28</td>
<td>0.202</td>
<td>0.483</td>
<td>15.5</td>
<td>1.38</td>
</tr>
<tr>
<td>434-8</td>
<td>450</td>
<td>0.222</td>
<td>1.54</td>
<td>3.61</td>
<td>0.382</td>
<td>1.64</td>
<td>12.7</td>
<td>1.34</td>
</tr>
<tr>
<td>434-8</td>
<td>2000</td>
<td>0.213</td>
<td>1.47</td>
<td>2.45</td>
<td>0.259</td>
<td>0.471</td>
<td>16.7</td>
<td>1.77</td>
</tr>
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</table>

\( A = \frac{\text{RCF}_3\text{H}/R^2\text{C}_2\text{F}_6}{\text{CD}_3\text{OH}} \); \( B = \frac{\text{RCF}_3\text{D}/R^2\text{C}_2\text{F}_6}{\text{CD}_3\text{OH}} \);

\( \text{CD}_3\text{OH} \) and TFMI in \( 10^{-6} \) mole cm\(^{-3} \); \( \text{CF}_3\text{H}, \text{CF}_3\text{D} \) and \( \text{C}_2\text{F}_6 \) in \( 10^{-12} \) mole cm\(^{-3} \) sec\(^{-1} \).

The formation of \( \text{CD}_3\text{H} \) and \( \text{CD}_4 \) suggests that the following displacement reaction occurs,

\[
\text{CF}_3 + \text{CD}_3\text{OH} \rightarrow \text{CF}_3\text{OH} + \text{CD}_3 ,
\]

followed by

\[
\text{CD}_3 + \text{CD}_3\text{OH} \rightarrow \text{CD}_3\text{H} + \text{CD}_2\text{O} \rightarrow \text{CD}_4 + \text{CD}_2\text{OH} .
\]

Table 4.—Hydrogen atom abstraction from methanol by trifluoromethyl radicals

<table>
<thead>
<tr>
<th>T°K</th>
<th>( t ) (sec)</th>
<th>( \text{CH}_3\text{OH} )</th>
<th>TFMI</th>
<th>( \text{CF}_3\text{H} )</th>
<th>( \text{CF}_3\text{D} )</th>
<th>( \text{C}_2\text{F}_6 )</th>
<th>( k_1/k_2^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>356-8</td>
<td>1200</td>
<td>0.496</td>
<td>1.38</td>
<td>3.69</td>
<td>0.073</td>
<td>0.743</td>
<td>8.7</td>
</tr>
<tr>
<td>357-0</td>
<td>1200</td>
<td>0.285</td>
<td>1.655</td>
<td>2.36</td>
<td>0.867</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>357-1</td>
<td>1800</td>
<td>0.369</td>
<td>1.49</td>
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<tr>
<td>413-6</td>
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<td>0.236</td>
<td>1.58</td>
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<td>6.32</td>
<td>0.937</td>
<td>17.1</td>
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<td>1.00</td>
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<td>0.826</td>
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<td>6.01</td>
<td>1.09</td>
<td>25.1</td>
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</tbody>
</table>

\( \text{CH}_3\text{OH} \) and TFMI in \( 10^{-6} \) mole cm\(^{-3} \); \( \text{CF}_3\text{H} \) and \( \text{C}_2\text{F}_6 \) in \( 10^{-12} \) mole cm\(^{-3} \) sec\(^{-1} \).

\( \text{CF}_3\text{H} \) and \( \text{C}_2\text{F}_6 \) formation in presence of \( \text{CH}_3\text{OH} \)

When the reaction of \( \text{CF}_3 \) radicals is carried out in the presence of unlabelled methanol, the \( \text{CF}_3\text{H} \) formation reveals only the overall rate of hydrogen atom abstraction from the alcohol, i.e., reaction (11) represents the sum of the individual reactions.
(12) and (13):

\[ \text{CF}_3 + \text{CH}_3\text{OH} \rightarrow \text{CF}_3\text{H} + (\text{H}_3\text{OC}) \]

\[ \rightarrow \text{CF}_3\text{H} + \text{CH}_3\text{O} \]

\[ \rightarrow \text{CF}_3\text{H} + \text{CH}_2\text{OH} \]

The overall velocity constant \( k_{11} \) is given by the relation:

\[ R_{\text{CF}_3\text{H}}/R_{2\text{E}_12}[\text{CH}_3\text{OH}] = k_{11}/k_3. \]

Our data are given in table 4 and are represented by the equation:

\[ \log k_{11} \left(\text{mole}^{-1} \cdot \text{cm}^3 \cdot \text{sec}^{-1}\right) = (9.92 \pm 0.15) - \left(3740 \pm 270\right)/2.3037T. \]

By making the assumption that \( k_{12} = k_9 \) (i.e., that there is no significant secondary isotope effect) we deduce the Arrhenius parameters for reaction (13). We find that

\[ \log k_{13} \left(\text{mole}^{-1} \cdot \text{cm}^3 \cdot \text{sec}^{-1}\right) = 10.0470/2.3037T. \]

**DISCUSSION**

**PRIMARY ISOTOPE EFFECTS IN CF\textsubscript{3} RADICAL ATTACK ON METHANOL**

The results enable a primary isotope effect to be determined for the CD\textsubscript{3}— and CH\textsubscript{3}— groups in methanol. Comparison of \( k_{10} \) and \( k_{13} \) indicates that a hydrogen atom is abstracted more readily than is a deuterium atom. The ratio \( k_{13}/k_{10} \) varies with temperature having a value of 6.3 at 164°C. Comparison of the equations for reactions (10) and (13) indicate that, within experimental error, the pre-exponential factors are equal. The activation energy difference \( E_{10} - E_{13} \) (\( = E_D - E_H \)) is 1.9 ± 0.6 kcal mole\textsuperscript{-1}. Within this large experimental scatter this difference is equal to the zero-point energy (z.p.e.) difference corresponding to a single C—H and C—D stretching vibration, i.e., 1.2 kcal mole\textsuperscript{-1}.

Below we compare data for the primary isotope effect for methanol using methyl \textsuperscript{11} and trifluoromethyl radicals.

<table>
<thead>
<tr>
<th>radical</th>
<th>substrates</th>
<th>( A_{\text{H}}/A_{\text{D}} )</th>
<th>( (E_{\text{H}} - E_{\text{D}}) )</th>
<th>( k_{13}/k_{10} ) (164°C)</th>
<th>z.p.e. diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF\textsubscript{3}</td>
<td>CD\textsubscript{3}OH, CH\textsubscript{3}OH</td>
<td>0.6</td>
<td>1.9</td>
<td>5.6</td>
<td>1.2</td>
</tr>
<tr>
<td>CH\textsubscript{3}</td>
<td>CD\textsubscript{3}OH, CH\textsubscript{3}OH</td>
<td>0.6</td>
<td>1.1</td>
<td>6.3</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**HYDROGEN ATOM ABSTRACTION FROM METHANOL**

A feature of our results for the reactions of CF\textsubscript{3} radicals with methanol is the low pre-exponential factor for the reaction involving breaking of the O—H bond, although the \( A \)-factor for breaking the C—H bond is about normal. Our data do not agree with those of Carlton et al. \textsuperscript{6} These workers used hexafluoroazomethane as their radical source and a competitive technique involving infra-red analysis of the reaction mixture to follow the reaction. They report the ratio [CF\textsubscript{3}D][CF\textsubscript{3}H] to have values varying from 1.08 at 107°C to 2.55 at 255°C. Our values vary from 0.05 at 84°C to 0.10 at 162°C. We have no explanation why these two sets of experimental data differ so considerably.

Since iodine atoms are present in the reaction system the following reaction sequence may contribute to the formation of CF\textsubscript{3}H and CF\textsubscript{3}D:

\[ \text{I} + \text{CD}_3\text{O} \rightarrow \text{DI} + \text{CD}_2\text{O} \]

\[ \text{CF}_3 + \text{DI} \rightarrow \text{CF}_3\text{D} + \text{I} \]

\[ \text{I} + \text{CD}_2\text{OH} \rightarrow \text{HI} + \text{CD}_2\text{O} \]

\[ \text{CF}_3 + \text{HI} \rightarrow \text{CF}_3\text{H} + \text{I}. \]
We consider it unlikely that reaction (15) or reaction (17) will occur so extensively as to explain the difference in \([CF_3D/|CF_3H]\) ratios mentioned above, particularly since Whittle in his study 12 of the photo-bromination of methanol has suggested that bromine atoms abstract hydrogen from the methyl groups of methanol. Similar behaviour with iodine atoms would lead to “extra” \(CF_3D\) formation, so that our ratios (0.05 at 84°C) represent an upper limit to the rate \([CF_3D/|CF_3H]\).

In addition, it is likely that any significant contribution of reactions (15) and (17) or the analogous reactions with \(CH_3OH\) would become apparent as variations in the appropriate rate constant ratios as the concentration ratio [alcohol]/[iodide] is altered. Tables 3 and 4 show no variation greater than to be expected on the basis of experimental deficiencies.

Table 5.—Comparison of Velocity Constants at 164°C and Arrhenius Parameters for Abstraction from Methanol by \(CF_3\) and \(CH_3\) Radicals

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\log A) (mole(^{-1}) cm(^3) sec(^{-1}))</th>
<th>(E) (kcal mole(^{-1}))</th>
<th>(\log k(164)) (mole(^{-1}) cm(^3) sec(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CF_3 + CH_3OH \rightarrow CF_3H)</td>
<td>9.92</td>
<td>3.7</td>
<td>8.07</td>
<td>this work</td>
</tr>
<tr>
<td>(CF_3 + CH_3OH \rightarrow CF_3H)</td>
<td>11.63</td>
<td>8.3</td>
<td>7.45</td>
<td>6</td>
</tr>
<tr>
<td>(CH_3 + CH_2OH \rightarrow CH_4)</td>
<td>10.68</td>
<td>8.4</td>
<td>6.48</td>
<td>11</td>
</tr>
<tr>
<td>(CD_3OH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CF_3 + CD_2OH \rightarrow CF_3D)</td>
<td>10.20</td>
<td>6.6</td>
<td>6.90</td>
<td>this work</td>
</tr>
<tr>
<td>(CF_3 + CD_2OH \rightarrow CF_3H)</td>
<td>9.48</td>
<td>3.2</td>
<td>7.88</td>
<td>this work</td>
</tr>
<tr>
<td>(CF_3 + CH_2OD \rightarrow CF_3H(CH_2OD))</td>
<td>11.6</td>
<td>8.3</td>
<td>7.45</td>
<td>6</td>
</tr>
<tr>
<td>(CH_3 + CH_2OD \rightarrow CH_3H(CH_2OD))</td>
<td>12.6</td>
<td>8.3</td>
<td>8.45</td>
<td>6</td>
</tr>
<tr>
<td>(CD_3 + CD_2OH \rightarrow CD_4)</td>
<td>10.18</td>
<td>9.3</td>
<td>5.53</td>
<td>11</td>
</tr>
<tr>
<td>(CD_3 + CD_2OH \rightarrow CD_3H)</td>
<td>10.46</td>
<td>9.0</td>
<td>5.96</td>
<td>11</td>
</tr>
</tbody>
</table>

In table 5 we have compared the Arrhenius parameters and velocity constants at 164°C (where 2.030 \(RT\) is 2000) for the \(CF_3+\) methanol and \(CH_3+\) methanol systems. It is clear that the trifluoromethyl radical abstracts hydrogen much more readily from both the C—H and O—H positions than does a methyl radical. With the methyl radical, at 164°C the \(CH_3\) group is about 1.8 times as reactive as the OH group in losing an hydrogen atom by abstraction. When \(CF_3\) is the abstracting radical the OH group is slightly more reactive (1.5 times) than the methyl group.

Deuterium atom abstraction from the alkyl group by trifluoromethyl radicals requires a lower activation energy (by 2.7 kcal mole\(^{-1}\)) than methyl radicals, although the pre-exponential factors for both reactions are similar. In addition, \(CF_3\) radicals abstract about 30 times more readily than methyl radicals from the alkyl group. This is analogous behaviour to that reported when these radicals react with alkanes, i.e., \(\Delta E \sim 3\) kcal mole\(^{-1}\), \(A_{CF_3} \sim A_{CH_3}\). For example, with ethane 13 as the substrate molecule, the Arrhenius parameters are \((CF_3)\), \(log A = 11.7\), \(E = 7.5\), and \((CH_3)\), \(log A = 11.1\), \(E = 10.4\) kcal mole\(^{-1}\), and \(k_{CF_3}/k_{CH_3} \sim 100\).

Hydrogen atom abstraction from the hydroxyl group shows marked differences between the two radicals, although again the polar radical is more reactive by a factor of ca. 90. The activation energy requirements differ by 5.8 kcal mole\(^{-1}\) and the \(A\)-factor for the reaction involving \(CF_3\) radicals is appreciably lower than the values frequently observed for such abstraction reactions. We consider that this may be explained as follows: to abstract the hydroxylic hydrogen atom the polar \(CF_3\) radical will be more restricted in its direction of approach for a collision leading to reaction than for abstraction of the hydrogen atom attached to the carbon atom. This is because of the strong repulsion forces which may be expected between the radical and the functional group of the methanol. Because of this effect there will
be a low steric factor, although if steric requirements are fulfilled there will be a high likelihood of reaction because of the low activation energy for reaction (12). Since attack on the alkyl group is not subject to such directional limitations a "normal" $A$-factor would be expected and is in fact observed. When methyl radicals react with methanol repulsion forces are not so marked and "normal" $A$-factors result.

**ABSTRACTION OF HYDROGEN IN CF$_3$H BY CH$_3$O RADICALS**

Rate constants and Arrhenius parameters for hydrogen atom abstractions reactions by methoxyl radicals from a variety of substrate molecules have been reported. By using data for reaction (12)

$$\text{CF}_3 + \text{CH}_3\text{OH} \rightarrow \text{CF}_3\text{H} + \text{CH}_3\text{O}$$

in conjunction with the equilibrium constant $K (= k_{12}/k_{-12})$ we obtain information regarding the reactivity of CH$_3$O radicals with fluoroform. Using the following entropy values $S_{298}$ (cal deg.$^{-1}$ mole$^{-1}$), (CH$_3$O) = 55, 14 (CF$_3$) = 60-7, 15 (CF$_3$H) = 62-0 15 and (CH$_3$OH) = 56-5, 16 we find that $\Delta S \approx 0$ cal deg.$^{-1}$ mole$^{-1}$, so that $A_{-12} = A_{12}$. To evaluate $E_{12}$ we need to know $\Delta H$ since $\Delta H = E_{12} - E_{-12}$. Using the JANAF values 15 for the heats of formation of CF$_3$ and CF$_3$H (viz., $-120-5$ and $-162-6$ kcal mole$^{-1}$ respectively) a value of about 94 kcal mole$^{-1}$ may be calculated for $D$(CF$_3$—H) which seems extremely low. Kerr 17 has suggested that Whittles' value 18 of 106 kcal mole$^{-1}$ is a more likely value. Using this value we find that $\Delta H = -4$ kcal mole$^{-1}$ and since $E_{12} = 3-2$ kcal mole$^{-1}$, then $E_{12}$ is 7-2 kcal mole$^{-1}$. The rate constant for reaction (—12) may therefore be represented by the equation:

$$\log k_{-12} \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 9-5 - 7200/2-303RT.$$

The rate constant so calculated is probably not accurate to better than an order or magnitude, but it does give a guide to the reactivity of the methoxyl radical.

We thank Laporte Chemical Co., for financial help towards this research.

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REACTIONS OF RADICALS CONTAINING FLUORINE

PART 2.—HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM
METHYLAMINE AND TRIDEUTEROMETHYLAMINE BY TRIFLUOROMETHYL
RADICALS

EXPERIMENTAL

The procedure of the reaction is similar to that described previously
for the reaction of methylamine with trifluoromethyl radicals.

A solution of 50% of 2,4-dinitrofluorobenzene in methanol is added
to a solution of the amine and trifluoromethyl radicals. The reaction
is allowed to proceed at room temperature for 24 hours. The
reaction mixture is then evaporated to dryness and the residue is
analyzed by gas chromatography. The product is identified by its
retention time on the gas chromatograph and by its infrared spectrum.
Reactions of Radicals Containing Fluorine

Part 2.—Hydrogen and Deuterium Atom Abstraction from Methylamine and Trideuteromethylamine by Trifluoromethyl Radicals.

By E. R. Morris and J. C. J. Thynne

Chemistry Dept., Edinburgh University.

Received 13th October, 1967

The reactions of trifluoromethyl radicals with methylamine and trideuteromethylamine have been studied in the temperature range 30-160°C in order to determine the rates at which hydrogen and deuterium atoms are abstracted from the molecules. With methylamine, radical attack is favoured at the alkyl position, and substitution of deuterium for hydrogen alters the positional reactivity by an amount in accord with the zero-point energy difference. The pre-exponential factors for attack at the nitrogen site have been explained in terms of a low steric factor due to repulsion forces between the polar molecule and the radical. Arrhenius parameters (based upon a value of $10^{13.34}$ mole$^{-1}$ cm$^3$ sec$^{-1}$ for the rate constant of combination of trifluoromethyl radicals) have been measured for the reactions:

\[
\begin{align*}
\text{CF}_3 + \text{CD}_3\text{NH}_2 & \rightarrow \text{CF}_3\text{H} + \text{CD}_3\text{NH} \\
\text{CF}_3 + \text{CD}_3\text{NH}_2 & \rightarrow \text{CF}_3\text{D} + \text{CD}_2\text{NH}_2 \\
\text{CF}_3 + \text{CH}_3\text{NH}_2 & \rightarrow \text{CF}_3\text{H} + (\text{CNH})_2 \\
\text{CF}_3 + \text{CH}_3\text{NH}_2 & \rightarrow \text{CF}_3\text{H} + \text{CH}_2\text{NH}_2
\end{align*}
\]

and have been calculated for

\[
\text{NHCH}_3 + \text{CF}_3\text{H} \rightarrow \text{NH}_2\text{CH}_3 + \text{CF}_3
\]

(units of $A$, mole$^{-1}$ cm$^3$ sec$^{-1}$; and $E$, kcal mole$^{-1}$).

The abstraction of hydrogen atoms from various hydrocarbons by trifluoromethyl radicals has been studied by several workers and in general it appears that such reactions proceed faster and have lower activation energy requirements than do the corresponding reactions involving alkyl radicals. There have been few studies of hydrogen atom abstraction reactions by fluoroalkyl radicals with molecules where there are abstractable hydrogen atoms attached to two different atoms, e.g., with methyl mercaptan or with methylamine. Since data are available for the reaction of methyl radicals with methylamine-d$_3$ and methylamine, it was decided to compare the reactivities of methyl and trifluoromethyl radicals with these substrates using trideuteromethylamine to evaluate the separate contributions involving the C—H and N—H bonds. Our results also enable a kinetic isotope effect to be assessed for the methyl and trideuteromethyl groups.

Experimental

The photolysis of hexafluoroacetone is frequently used as a convenient source of trifluoromethyl radicals in hydrogen-atom abstraction studies. With substrates such as methylamine hexafluoroacetone reacts rapidly to form a rather involatile solid. Trifluoromethyl iodide (TFMI) does not react with these compounds and accordingly we have chosen the photolysis of TFMI as our radical course. TFMI has another advantage, that secondary reactions between trifluoromethyl radicals and the radical species R formed in the initial hydrogen atom abstraction

\[
\text{CF}_3 + \text{RH} \rightarrow \text{CF}_3\text{H} + \text{R}
\]

are reduced or inhibited by the iodine present in the reacting system.
TRIFLUOROMETHYL IODIDE was prepared by heating a 1:3 intimate mixture of silver trifluoroacetate (Koch-Light) and iodine in a closed system under slightly reduced pressure and collecting the gas evolved in a series of cold traps. Impurities such as fluoroform, hexafluoroethane and carbon dioxide were removed by extensive pumping at $-130^\circ\text{C}$ on a vacuum line.

TRIDEEUTEROMETHYLAMINE was prepared from the hydrochloride salt (E. Merck A. G. Darmstadt) by dropping potassium hydroxide solution on the salt and collecting the gas evolved from the warmed solution. It was further purified by fractionating several times at $-78^\circ\text{C}$ before storage on the vacuum line.

METHYLAMINE was similarly prepared from the hydrochloride.

### MATERIALS

### RESULTS AND DISCUSSION

**CF$_3$H and C$_2$F$_6$ formation during photolysis of TFMI in the presence of trideuteromethylamine**

When trifluoromethyl radicals, generated by the photolysis of trifluoromethyl iodide, react with trideuteromethylamine, CF$_3$H, CF$_3$D and C$_2$F$_6$ are observed as reaction products and they are accounted for by the following reaction scheme:

1. $\text{CF}_3 + \text{CD}_3\text{NH}_2 \rightarrow \text{CF}_3\text{H} + \text{CD}_3\text{NH}$
2. $\text{CF}_3\text{D} + \text{CD}_2\text{NH}_2$
3. $2\text{CF}_3 \rightarrow \text{C}_2\text{F}_6$

### APPARATUS AND PROCEDURE

The essential details of the apparatus used and the analytical technique employed have been described. Decomposition of the substrate was usually 1-2%.

### Table 1.—Hydrogen and deuterium atom abstraction from trideuteromethylamine by trifluoromethyl radicals.

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>t (sec)</th>
<th>CD$_3$NH$_2$</th>
<th>CF$_3$H</th>
<th>CF$_3$D</th>
<th>C$_2$F$_6$</th>
<th>$k_1/k_2$</th>
<th>$k_2/k_3$</th>
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<td>4-42</td>
<td>7-21</td>
<td>2-44</td>
<td>4-33</td>
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<tr>
<td>400-0</td>
<td>500</td>
<td>0-57</td>
<td>0-59</td>
<td>7-86</td>
<td>13-0</td>
<td>4-03</td>
<td>6-85</td>
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<tr>
<td>416-6</td>
<td>150</td>
<td>0-96</td>
<td>1-01</td>
<td>19-2</td>
<td>25-9</td>
<td>2-89</td>
<td>11-7</td>
</tr>
<tr>
<td>434-8</td>
<td>450</td>
<td>0-53</td>
<td>0-60</td>
<td>14-9</td>
<td>22-5</td>
<td>3-71</td>
<td>14-4</td>
</tr>
<tr>
<td>434-8</td>
<td>450</td>
<td>0-60</td>
<td>0-82</td>
<td>14-1</td>
<td>23-5</td>
<td>2-95</td>
<td>13-7</td>
</tr>
</tbody>
</table>

CD$_3$NH$_2$ and CF$_3$I in $10^6$ mole cm$^{-3}$.

CF$_3$H, CF$_3$D and C$_2$F$_6$ in $10^{12}$ mole cm$^{-3}$ sec$^{-1}$. 

as reaction products and they are accounted for by the following reaction scheme.
and the following steady-state equations apply:

\[ \frac{R_{CF_3H}}{R_{CF_3D}} = \frac{k_1}{k_3} \quad \text{and} \quad \frac{R_{CF_3}[CD_3NH_2]}{R_{CF_3}[CD_3NH_2]} = \frac{k_2}{k_3} \]

where \([CD_3NH_2]\) denotes the concentration of trideuteromethylamine and \(R_X\) the rate of formation of \(X\).

Our results are shown in table 1. When treated by the method of least-mean-squares they are represented by the equations:

\[ \log k_1 \ (\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (9-94 \pm 0-22) - (4390 \pm 370)/2-303 \text{ RT} \]

and

\[ \log k_2 \ (\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (11-03 \pm 0-09) - (6050 \pm 160)/2-303 \text{ RT} \]

The error limits quoted represent the standard deviations of a least-mean-squares computer treatment.

We have used the value of \(10^{13.34} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}\) obtained by Ayscough \(^6\) for the rate constant \(k_3\) for the combination of trifluoromethyl radicals. There are no Arrhenius parameters reported for the above reactions with which our values may be compared.

**IN THE PRESENCE OF METHYLMETHYLENE**

When trifluoromethyl iodide is photolyzed in the presence of unlabelled methyamine, the fluoroform formation indicates only the total attack of trifluoromethyl radicals on the substrate, i.e., reaction (4) represents the sum of the individual reactions (5) and (6). Hence \(k_4\) is not a meaningful velocity constant, being a composite value of \(k_5\) and \(k_6\):

\[ \begin{align*}
\text{CF}_3 + \text{CH}_3\text{NH}_2 & \rightarrow \text{CF}_3\text{H} + (\text{CNH}_4) \\
\text{CF}_3\text{H} & \rightarrow \text{CF}_3\text{H} + \text{CH}_3\text{NH} \\
\text{CF}_3\text{H} & \rightarrow \text{CF}_3\text{H} + \text{CH}_2\text{NH}_2.
\end{align*} \]

Our data are reported in table 2 and for the overall velocity constant \(k_4\) are represented by

\[ \log k_4 \ (\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (10-79 \pm 0-16) - (4190 \pm 260)/2-303 \text{ RT} \]

Secondary isotope effects are usually insignificant \(^7-9\) in reactions such as those quoted above. If the secondary isotope effect is zero \(^4\) then the difference in the velocity constants for \(\text{CF}_3\text{H}\) formation from \(\text{CH}_3\text{NH}_2\) and \(\text{CD}_3\text{NH}_2\) equals the velocity constant \(k_6\) for \(\text{CF}_3\text{H}\) formation by attack on the methyl group in \(\text{CH}_3\text{NH}_2\).

With the assumption that \(k_1 = k_5\), we find that

\[ \log k_6 \ (\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = (10-72 \pm 0-39) - (4170 \pm 650)/2-303 \text{ RT} \]

Evaluation of the velocity constants \(k_3\) and \(k_6\) enable a quantitative comparison of the reactivity of the hydrogen atoms in the amino and methyl groups of methyamine to be made. The methyl group is more reactive towards radical attack, at 164°C (where 2-303 \(\text{RT}\) is 2000) \(k_4\) and \(k_6\) having values of \(10^{7.7}\) and \(10^{8.6}\) \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}\) respectively. Hence at this temperature for every eight hydrogen atoms abstracted seven come from the methyl group. This is in sharp contrast with the results reported for methyl radical attack on methyamine which indicate (see table 3) that the methyl and amino groups have similar reactivities (on an overall basis) at 164°C. In terms of the number of hydrogen atoms available for reaction, the amino group is slightly the more reactive. For methanol the methyl group is less reactive than the hydroxyl.
group (on a per-atom basis) towards attack by both methyl and trifluoromethyl and again the difference is most apparent with the polar radical.

Pritchard et al.² have shown that, for many hydrocarbons, the activation energies required for hydrogen atom abstraction by trifluoromethyl radicals are ~3-4 kcal mole⁻¹. Hydrogen atom abstraction from methylamine by trifluoromethyl radicals has been studied, and the reaction rates for various reactions are given below.

### Table 2: Hydrogen Atom Abstraction Form Methylamine by Trifluoromethyl Radicals

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log A (mole⁻¹ cm³ sec⁻¹)</th>
<th>E (kcal mole⁻¹)</th>
<th>kₐ/kₐ⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃ + CH₄ → CF₃H + CH₃</td>
<td>10⁻³</td>
<td>6-6</td>
<td>6-0</td>
</tr>
<tr>
<td>CH₃ + CH₄ → CH₄ + CH₃</td>
<td>10⁻⁴</td>
<td>8-0</td>
<td>7-5</td>
</tr>
<tr>
<td>CF₃ + CD₃NH₂ → CF₃D + CD₂NH₂</td>
<td>10⁻²</td>
<td>6-1</td>
<td>8-0</td>
</tr>
<tr>
<td>CF₃ + CD₃NH₂ → CF₃H + CD₂NH₂</td>
<td>10⁻²</td>
<td>6-1</td>
<td>8-0</td>
</tr>
<tr>
<td>CF₃ + CH₃OH → CF₃H + CH₂OH</td>
<td>10⁻²</td>
<td>4-7</td>
<td>7-7</td>
</tr>
<tr>
<td>CH₃ + CH₃OH → CH₄ + CD₂O</td>
<td>10⁻³</td>
<td>4-7</td>
<td>7-7</td>
</tr>
<tr>
<td>CF₃ + CH₃OH → CF₃H + CH₂OH</td>
<td>10⁻³</td>
<td>4-7</td>
<td>7-7</td>
</tr>
<tr>
<td>CF₃ + CH₂OH → CF₃H + CH₂OH</td>
<td>10⁻³</td>
<td>4-7</td>
<td>7-7</td>
</tr>
<tr>
<td>CH₃ + CH₂OH → CH₄ + CD₂O</td>
<td>10⁻³</td>
<td>4-7</td>
<td>7-7</td>
</tr>
<tr>
<td>CF₃ + CH₃CD₂ → CF₃H + CD₂H₂</td>
<td>11⁻¹</td>
<td>7-5</td>
<td>7-9</td>
</tr>
<tr>
<td>CH₃ + CH₃CD₂ → CH₄ + CD₂H₂</td>
<td>11⁻¹</td>
<td>7-5</td>
<td>7-9</td>
</tr>
</tbody>
</table>

The hydrogen atom which is abstracted is underlined for methylamine, methanol and ethane-d₃. mole⁻¹ lower and the reaction rates much higher than for the corresponding reactions involving methyl radicals. Comparison of the Arrhenius parameters determined for reaction (6) with the values established for the reaction

\[ CH₃ + CH₃NH₂ → CH₄ + CH₂NH₂ \]
shows that the pre-exponential factors are similar (10.73 and 10.99 respectively) but there is an activation energy difference of about 4.5 kcal mole\(^{-1}\), so that the alkyl group in a polar molecule behaves in a similar manner as in a hydrocarbon, i.e., there is a lowering of the activation energy required for abstraction by the CF\(_3\) radical.

Of particular interest is the pre-exponential factor for reaction (1) which is lower than the values frequently reported for hydrogen atom abstraction reactions, particularly with hydrocarbon substrates. Benson and DeMore have suggested that such values are the result of the occurrence of secondary reactions between the primary radical and the product radical. We consider this not to be the explanation for such values partly because of the small extent of reaction (1-2 \%) and because variation of the [TFMI]/[CH\(_3\)NH\(_2\)] ratio over a thirty-fold range showed no variation in the rate constant ratio outside that attributable to the experimental error involved in measuring small quantities of C\(_2\)F\(_6\). Also, variation in the reaction times by a factor of ten showed no alteration in the rate constant ratio. In addition, a study of the reaction of trifluoromethyl radicals with n-butane has indicated that the occurrence of facile secondary reactions does not give rise to such low pre-exponential factors. Unpublished results obtained in this laboratory have indicated similar behaviour with cyclohexane.

An investigation of the reaction of trifluoromethyl radicals with methanol has shown that a similar situation exists for this molecule, i.e., a "normal" pre-exponential factor for attack on the methyl group and a "low value" (10\(^{-5}\)) for the hydroxyl group. We consider that the results for methanol and methylamine may be interpreted in terms of the strong repulsion forces which are likely between the polar radical and the function group of the substrate molecule. Because of this, the polar radical will be restricted in its approach to the molecule for a reactive collision involving the functional group, and as a consequence there will be a low steric factor for such a reaction. If steric conditions are satisfied there will be a high likelihood of reaction because the activation energy requirements are small. Attack on the methyl group of the polar molecule is not so subject to steric limitations and hence "normal" pre-exponential factors are to be expected and are observed.

**PRIMARY ISOTOPE EFFECTS IN CF\(_3\) RADICAL ATTACK ON METHYLAMINE**

The results reported above enable a primary kinetic isotope effect to be deduced for the methyl and trideuteromethyl groups in methylamine. Comparison of the velocity constants \(k_2\) and \(k_6\) shows that a hydrogen atom is abstracted more readily than is a deuterium atom, the ratio \(k_6/k_2\) varying with temperature with a value of 4.1 at 164°C.

Below we have compared our data for the primary isotope effect with results reported for several similar substrates for methyl and trifluoromethyl radicals. In all cases the ratio \(A_H/A_D\) is near to the expected value of unity, though the fact that in the examples the ratio is slightly less than one may not be significant since the deviation is within the experimental error in all cases. Activation energy differences,
$E_D - E_H$, are close to the zero-point energy difference (z.p.e.) of 1.2 kcal mole$^{-1}$ corresponding to a single C—H and C—D stretching vibration.

**REACTIONS OF NH$_3$ RADICALS**

There are few kinetic data available for nitrogen containing radicals, particularly regarding their ability to abstract hydrogen atoms from substrate molecules. This is partly due to the experimental difficulties inherent in direct studies of such reactions. It is possible, however, to determine such data indirectly from a study of the reverse reaction in conjunction with a knowledge of the thermodynamics of the overall reaction since the Arrhenius parameters of the forward and back reactions are related $^{12}$ by the expressions:

$$\log \left( \frac{A_f}{A_b} \right) = \Delta S^0/2 \cdot 303 R, \text{ and } E_f - E_b = \Delta H^0.$$  

By using the data reported above for reaction (1) we can evaluate the Arrhenius parameters for reaction (7),

$$\text{NHCH}_3 + \text{CF}_3\text{H} \rightarrow \text{NH}_2\text{CH}_3 + \text{CF}_3,$$

where the methylamino radicals abstract hydrogen from fluoroform.

Using the following entropy values, $S^0_298$ (cal deg.$^{-1}$ mole$^{-1}$), (NH$_3$) = 56.4$^3$, (NH$_2$CH$_3$) = 57.7$^{13}$ (CF$_3$) = 60.7$^{14}$ and (CF$_3$H) = 62.0$^{14}$ we find that for reaction (7) the overall entropy change $\Delta S^0$ is close to zero, i.e., $A_1 = A_7$.

The enthalpy change $\Delta H^0$ is related to the difference between the strengths of the bonds formed and broken and hence depends on $D$(CF$_3$—H). Although no direct determination has been made it seems well established $^{15}$ that Whittle’s value $^{16}$ of 106 kcal mole$^{-1}$ is likely to be accurate. Using this value together with the value $^{19}$ of 92 kcal mole$^{-1}$ reported for $D$(CH$_3$NH—H), we find that the velocity constant for reaction (7) is represented by the equation:

$$\log k_7 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 9.9 - 18400/2 \cdot 303 RT.$$  

The rate constant calculated in this manner is probably not accurate to better than an order of magnitude but the equation gives a guide to the relative reactivities of the radical.

We thank Laporte Chemicals Ltd., for financial aid.

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REACTIONS OF RADICALS CONTAINING FLUORINE
PART 3.—HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM DIMETHYLAMINE, DIMETHYLAMINE-D, TRIMETHYLAMINE AND ETHYLENEIMINE
Reactions of Radicals containing Fluorine

Part 3.—Hydrogen and Deuterium Atom Abstraction from Dimethylamine, Dimethylamine-d, Trimethylamine and Ethylenimine

BY E. R. MORRIS AND J. C. J. THYNNE,
Chemistry Dept., Edinburgh University

Received 17th April, 1968

The reactions of trifluoromethyl radicals with dimethylamine, dimethylamine-d, trimethylamine and ethylenimine have been studied in the temperature range 27-161°C. Arrhenius parameters (based upon a value of $10^{-13.37}$ mole$^{-1}$ cm$^3$ sec$^{-1}$ for the velocity constant for the combination of trifluoromethyl radicals) have been obtained for the reactions:

- $\text{CF}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_2\text{N} \quad \log_{10} k = 11.45 \pm 0.12, \quad E = 4.1 \pm 0.2$
- $\text{CF}_3 + (\text{CH}_3)_2\text{ND} \rightarrow \text{CF}_3\text{D} + (\text{CH}_3)_2\text{N} \quad \log_{10} k = 10.88 \pm 0.29, \quad E = 4.7 \pm 0.5$
- $\text{CF}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_2\text{N} \quad \log_{10} k = 10.5 \pm 0.7, \quad E = 3.3 \pm 1.0$
- $\text{CF}_3 + (\text{CH}_3)_2\text{ND} \rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_2\text{ND} \quad \log_{10} k = 11.82 \pm 0.51, \quad E = 5.1 \pm 0.8$
- $\text{CF}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_2\text{NCH}_2 \quad \log_{10} k = 11.82 \pm 0.12, \quad E = 4.5 \pm 0.2$
- $\text{CF}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_2\text{H} \quad \log_{10} k = 11.00 \pm 0.17, \quad E = 4.1 \pm 0.3$

With dimethylamine, radical attack is favoured, on a "per-atom basis," at the nitrogen atom but the difference in reactivities of the C—H and N—H bonds is much less marked than with methyl radicals. Assuming a zero secondary isotope effect, substitution of D for H in dimethylamine alters the reactivity of the amino group by an amount in accord with zero-point-energy difference.

The reactions of methyl radicals with a wide variety of nitrogen-containing compounds have been studied$^{1-5}$ and information obtained regarding the positions and rates of hydrogen atom abstraction from the substrates. Trifluoromethyl radicals also readily abstract hydrogen from such molecules and their reactions with trideuteromethylamine and methylamine have been examined.$^6$ We have extended this investigation to dimethylamine, trimethylamine and ethylenimine.

EXPERIMENTAL

The apparatus used and experimental technique employed have been described.$^7$

MATERIALS. Dimethylamine, trimethylamine and ethylenimine were commercial samples which were purified by low-temperature distillation on the vacuum line.

Dimethylamine-d was prepared by shaking dimethylamine with acidified D$_2$O at 25°C for 24 h followed by low-temperature distillation. This procedure was repeated and the extent of deuteration was followed by measuring the 730 cm$^{-1}$ band in the infra-red spectrum which shifts to 587 cm$^{-1}$ on deuteration. The sample was dried by low-temperature bulb-to-bulb distillation before being stored on the vacuum line. The sample used contained 63 % dimethylamine-d$_1$.

RESULTS

Hexafluoroacetone is frequently used as a photochemical source of trifluoromethyl radicals; however, it reacts to form a white involatile solid with amines. We have chosen the photolysis of trifluoromethyl iodide (TFMI) as the source of free radicals since no reaction (as evidenced by there being no pressure change) occurred when this was mixed with any of the compounds used in this investigation.
PHOTOLYSIS OF TFMI IN THE PRESENCE OF TRIMETHYLAMINE

When TFMI is photolyzed in the presence of trimethylamine the reaction products observed and analyzed were CF$_3$I and C$_2$F$_6$. Their formation and distribution are accounted for by reactions (1) and (2):

1. $^1$CF$_3$ + (CH$_3$)$_3$N $\rightarrow$ CF$_3$H + (CH$_3$)$_2$NCH$_2$

2. 2 CF$_3$ $\rightarrow$ C$_2$F$_6$.

The following relationship may be derived:

$$R_{CF_3H}/R_{C_2F_6}[(CH_3)_3N] = k_1/k_2,$$

where $R_X$ refers to the rate of formation of X and $[(CH_3)_3N]$ is the mean concentration of trimethylamine. Our experimental data are shown in Table 1.

If a value of $10^{13.37}$ (mole$^{-1}$ cm$^3$ sec$^{-1}$) is used for the rate constant for the combination of trifluoromethyl radicals, our results are expressed by the equation:

$$\log k_1$$ (mole$^{-1}$ cm$^3$ sec$^{-1}$) = 11.85 ± 0.12 − (4460 ± 190)/2.303 $RT$,

where the error limits represent the standard deviation of a least-mean-squares computer treatment. The uncertainty in $k_2$ (~10$^{±0.2}$) has not been included in the error limits quoted in this paper.

<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>$t$ (sec)</th>
<th>$[(CH_3)_3N]$</th>
<th>$[CF_3I]$</th>
<th>$[CF_3H]$</th>
<th>$[C_2F_6]$</th>
<th>$k_1/k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303-0</td>
<td>100</td>
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<td>1.761</td>
<td>67.1</td>
<td>18.8</td>
<td>88.6</td>
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<td>1.008</td>
<td>1.003</td>
<td>39.0-2</td>
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<td>83.3</td>
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<td>322.5</td>
<td>100</td>
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<td>1.651</td>
<td>93.9</td>
<td>14.6</td>
<td>150</td>
</tr>
<tr>
<td>344.8</td>
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<td>230</td>
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<tr>
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<td>1.110</td>
<td>1008</td>
<td>10.6</td>
<td>277</td>
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<td>1.192</td>
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<td>0.305</td>
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<td>568</td>
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<tr>
<td>434.8</td>
<td>30</td>
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<td>1.586</td>
<td>1215</td>
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<td>879</td>
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<td>434.8</td>
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<td>1.091</td>
<td>683.5</td>
<td>9.95</td>
<td>813</td>
</tr>
</tbody>
</table>

(CH$_3$)$_3$N and CF$_3$I in 10$^6$ mole cm$^{-3}$; CF$_3$H and C$_2$F$_6$ in 10$^{12}$ mole cm$^{-3}$ sec$^{-1}$; $k_1/k_2$ in mole$^{-1}$ cm$^2$ sec$^{-1}$.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF ETHYLENEIMINE

Since in ethyleneimine hydrogen atoms are attached to the carbon and also to the nitrogen atoms, it is probable that CF$_3$H formation can occur by trifluoromethyl radical attack at both sites, i.e., reaction (3) represents the sum of the contributions from reactions (4) and (5).

$$CF_3 + (CH_2)_2NH \rightarrow CF_3H + C_2NH_4$$

$$\rightarrow CF_3H + CH_2(CH)NH$$

$$\rightarrow CF_3H + (CH_2)_2N.$$

Gray and Jones have studied the reaction of methyl radicals with ethyleneimine and, using a deuterium-labelling technique, have concluded that at 150°C the hydrogen
atom attached to the nitrogen atom is about 160 times more reactive than the corresponding hydrogen atom linked to the carbon atom. We have assumed that a similar situation exists for trifluoromethyl radicals and that data obtained for the overall-reaction represents closely the abstraction from the N—H bond, i.e., that \( k_3 = k_5 \).

Our experimental data are recorded in table 2 and are represented by the expression:

\[
\log k_3(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11.03 \pm 0.17 - (4140 \pm 270)/2.303 \text{ RT}.
\]

**Table 2.—Hydrogen atom abstraction from ethyleneimine by trifluoromethyl radicals**

<table>
<thead>
<tr>
<th>( T(\text{K}) )</th>
<th>( t(\text{sec}) )</th>
<th>( [(\text{CH}_2)_2\text{NH}] )</th>
<th>( [(\text{CF}_3)\text{I}] )</th>
<th>( [(\text{CF}_3)\text{H}] )</th>
<th>( [(\text{CF}_3)\text{D}] )</th>
<th>( k_3/k_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.1</td>
<td>45</td>
<td>0.429</td>
<td>1.758</td>
<td>57.3</td>
<td>40.6</td>
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</tr>
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<td>1.951</td>
<td>0.771</td>
<td>110.2</td>
<td>3.94</td>
<td>28.5</td>
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<td>59.7</td>
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<td>51.4</td>
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<tr>
<td>370.3</td>
<td>45</td>
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<td>1.575</td>
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<td>26.9</td>
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<td>86.3</td>
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<tr>
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<td>0.387</td>
<td>1.588</td>
<td>470.0</td>
<td>55.2</td>
<td>163</td>
</tr>
<tr>
<td>434.8</td>
<td>90</td>
<td>0.540</td>
<td>1.032</td>
<td>296.5</td>
<td>9.19</td>
<td>180</td>
</tr>
</tbody>
</table>

(CH\(_2\)\(_2\)NH and CF\(_3\)I in 10\(^6\) mole cm\(^{-3}\); CF\(_3\)H and C\(_2\)F\(_6\) in 10\(^{12}\) mole cm\(^{-3}\) sec\(^{-1}\); \( k_3/k_5 \) in mole\(^{-1}\) cm\(^3\) sec\(^{-4}\).

**Photolysis of TFMI in the presence of dimethylamine**

\[
\text{CF}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H} + \text{C}_2\text{H}_6\text{N}
\]

\[
\rightarrow \text{CF}_3\text{H} + \text{CH}_3(\text{CH}_2)\text{NH}
\]

\[
\rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_2\text{N}
\]

Hydrogen atom abstraction occur from both the C—H and N—H bonds, so that reaction (6) represents the overall sum of the contributions of reactions (7) and (8). Our results for the overall abstraction are given in table 3 and are expressed by

\[
\log k_6(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11.48 \pm 0.12 - (4140 \pm 180)/2.303 \text{ RT}.
\]

A study of the reaction of methyl radicals with dimethylamine \(^3\) has shown that, unlike for ethyleneimine, there is not such a large difference between the reactivity of the hydrogen atoms attached to the carbon and nitrogen atoms. Consequently, the individual contributions of reactions (7) and (8) may only be assessed by suitable labelling of dimethylamine.

We have investigated the reaction of CF\(_3\) radicals with dimethylamine-d\(_1\) containing 37 % (CH\(_3\)\(_2\)NH, and measured the CF\(_3\)H and CF\(_3\)D produced by reactions (9) and (10):

\[
\text{CF}_3 + (\text{CH}_3)_2\text{ND} \rightarrow \text{CF}_3\text{D} + (\text{CH}_3)_2\text{N}
\]

\[
\rightarrow \text{CF}_3\text{H} + \text{CH}_3(\text{CH}_2)\text{ND}.
\]

A correction was made for the CF\(_3\)H formed by reaction with the unlabelled amine (reaction (6)) before a comparison may be made between reactions (9) and (10).
This correction, together with the facts that the yield of CF₃D is generally much less than that of CF₃H and that relatively small amounts of C₂F₆ are formed, results in our data being subject to a large experimental error. Our data are shown in Table 4 and, after least-squares analysis, are expressed by the equations:

\[
\log k_8(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 10.91 \pm 0.29 - (4710 \pm 460)/2.303 \text{ RT},
\]

and

\[
\log k_{10}(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11.85 \pm 0.51 - (5060 \pm 820)/2.303 \text{ RT}.
\]

Table 3.—Hydrogen atom abstraction from dimethylamine by trifluoromethyl radicals

<table>
<thead>
<tr>
<th>T(K)</th>
<th>t(sec)</th>
<th>[(CH₃)₂NH]</th>
<th>[CF₃I]</th>
<th>[CF₃H]</th>
<th>[C₂F₆]</th>
<th>(k_6/k_7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>370-3</td>
<td>90</td>
<td>0.295</td>
<td>0.767</td>
<td>228</td>
<td>14.5</td>
<td>211</td>
</tr>
<tr>
<td>370-3</td>
<td>45</td>
<td>0.554</td>
<td>0.794</td>
<td>357</td>
<td>8.53</td>
<td>224</td>
</tr>
<tr>
<td>357-1</td>
<td>90</td>
<td>0.694</td>
<td>0.690</td>
<td>44.1</td>
<td>0.14</td>
<td>170</td>
</tr>
<tr>
<td>344-8</td>
<td>300</td>
<td>0.183</td>
<td>1.83</td>
<td>25.8</td>
<td>0.84</td>
<td>156</td>
</tr>
<tr>
<td>344-8</td>
<td>900</td>
<td>0.187</td>
<td>1.87</td>
<td>28.6</td>
<td>1.28</td>
<td>145</td>
</tr>
<tr>
<td>333-3</td>
<td>150</td>
<td>1.25</td>
<td>1.26</td>
<td>193</td>
<td>2.12</td>
<td>107</td>
</tr>
<tr>
<td>333-3</td>
<td>45</td>
<td>0.481</td>
<td>1.25</td>
<td>328</td>
<td>40.6</td>
<td>108</td>
</tr>
<tr>
<td>333-3</td>
<td>45</td>
<td>0.902</td>
<td>1.29</td>
<td>490</td>
<td>27.1</td>
<td>106</td>
</tr>
<tr>
<td>322-6</td>
<td>1100</td>
<td>0.124</td>
<td>1.24</td>
<td>11.5</td>
<td>1.02</td>
<td>96.5</td>
</tr>
<tr>
<td>322-6</td>
<td>90</td>
<td>0.479</td>
<td>1.36</td>
<td>30.3</td>
<td>0.52</td>
<td>88.6</td>
</tr>
<tr>
<td>322-6</td>
<td>900</td>
<td>0.476</td>
<td>1.35</td>
<td>31.7</td>
<td>0.45</td>
<td>102</td>
</tr>
<tr>
<td>312-7</td>
<td>90</td>
<td>0.591</td>
<td>1.54</td>
<td>307</td>
<td>54.2</td>
<td>72.2</td>
</tr>
<tr>
<td>303-0</td>
<td>300</td>
<td>0.345</td>
<td>1.66</td>
<td>18.8</td>
<td>0.75</td>
<td>63.5</td>
</tr>
<tr>
<td>303-0</td>
<td>1500</td>
<td>0.359</td>
<td>1.73</td>
<td>13.8</td>
<td>0.39</td>
<td>63.5</td>
</tr>
</tbody>
</table>

We can derive Arrhenius parameters for reaction (8) using our results for reactions (6) and (10) if we assume that secondary isotope effects are insignificant, i.e., \(k_7 = k_{10}\). Our data indicate that the velocity constant, \(k_8\), is expressed by

\[
\log k_8(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 10.5 \pm 0.7 - (3300 \pm 1000)/2.303 \text{ RT}.
\]
DISCUSSION

PRIMARY ISOTOPE EFFECT

Our results enable a primary isotope effect to be deduced for trifluoromethyl radical attack on the N—H and N—D bonds in dimethylamine and dimethylamine-d. Comparison of $k_8$ and $k_D$ indicates that hydrogen atom abstraction occurs more readily than that of a deuterium atom, the velocity constant ratio $k_8/k_D$ having a value of approximately 3 at 77°C. Comparison of the Arrhenius parameters for reactions (8) and (9) indicate that, within the appreciable experimental error, the pre-exponential factors are similar. The difference in reactivity of the N—H and N—D arises mainly because of the difference in the activation energy requirements. This difference, although subject to a large experimental error, is comparable with the zero-point energy difference $\Delta E_0$ of 1.3 kcal mole$^{-1}$, corresponding to a single N—H and N—D vibration. This observation is in accord with the primary isotope effects reported for several other systems involving methyl or trifluoromethyl radicals.1, 2, 6

COMPARISON OF REACTIVITY OF METHYL AND AMINO GROUPS
IN DIMETHYLAMINE

Knowledge of the velocity constants for reactions (10) and (8) enable a quantitative comparison of the ease of hydrogen atom abstraction from the methyl and amino groups in dimethylamine. Attack on the N—H bond, which is weaker than the C—H bond, requires the lower activation energy by ~1.7 kcal mole$^{-1}$. The pre-exponential factors differ by about an order of magnitude being “normal” for abstraction from the alkyl group but lower for the amino group. Similar behaviour has been reported for methanol 7 and methylamine 6 and was interpreted in terms of the repulsion forces likely between the polar radical and the functional group of the molecule, thereby restricting the radical in its approach to the molecule for a reactive collision.

At 164°C the ratio of velocity constants $k_10/k_8$ is ~3 so that the methyl group is more reactive on an overall basis than is the amino group. On a per-hydrogen-atom-available basis, however, the hydrogen attached to the nitrogen is about twice as reactive as the hydrogen linked to the carbon atom. When methyl radicals are the abstracting species 3 the ratio of velocity constants is about 18, the N—H bond being the more reactive. The trifluoromethyl radical is markedly less selective in abstracting hydrogen than is the methyl radical and this is in keeping with the greater reactivity of the trifluoromethyl radical.

REACTIVITY OF N—H BONDS IN CH$_3$NH$_2$, (CH$_3$)$_2$NH AND (CH$_2$)$_3$NH

In table 5 we have compared kinetic data for the abstraction of hydrogen from various substrates by methyl and trifluoromethyl radicals. In general, a similar pattern of reactivity is noted for both radicals, there being an increase in reactivity with decreasing bond strength, and activation energy requirements are ca. 1.5 kcal mole$^{-1}$ lower for the trifluoromethyl radical attack on the N—H bonds. With methylamine and dimethylamine, the introduction of a second methyl group has the effect of markedly increasing the reactivity of the N—H bond towards attack by both CH$_3$ and CF$_3$ radicals.

REACTIVITY OF C—H BONDS IN CH$_3$NH$_2$, (CH$_3$)$_2$NH AND (CH$_3$)$_3$N

The velocity constants for the abstraction of hydrogen attached to carbon increases as more hydrogen atoms are available in the molecule. For the series methylamine,
dimethylamine and trimethylamine, the velocity constants are in the ratio $1:4.5:10$ for CF$_3$ attack and $1:3:6$ for CH$_3$ attack. On a per-atom available basis the ratios are $1:2:3.5$ and $1:1.5:2$ respectively so that it appears that the $-$NH$_2$, $>$NH and $>$N groups do not have any marked difference in the activation of the C–H bonds. Within experimental error there is little difference in the activation energies; the activation energies for abstraction from C–H bonds are about 4 kcal mole$^{-1}$ lower for trifluoromethyl radicals than for methyl radicals. Pritchard et al.\textsuperscript{10} have reported that for abstraction from hydrocarbons there is an activation energy difference of about 3 kcal mole$^{-1}$.

The hydrogen atom which is abstracted is underlined.

We thank Laporte Chemicals Ltd., for financial aid.

The Thermal Decomposition of Dimethyl Azodiformate

by A. Jones,
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The thermal decomposition in the gas and liquid phases of compounds of the type \( \text{RN} = \text{NR} \) to yield nitrogen and the free radical \( R \) is well known, data having been reported for systems where \( R \) is an alkyl,\(^{1}\) alkoxyl,\(^{2}\) or alkylamino\(^{3}\) substituent.

\[ \text{RN} = \text{NR} \rightarrow \text{N}_2 + 2\text{R} \]  \( \text{(1)} \)

The decompositions of formates\(^{4-6}\) and carbonates\(^{6}\) have demonstrated the instability of alkoxyoxycarbonyl radicals, \( \text{COOR} \), which appear to decarboxylate quantitatively to generate an alkyl radical and carbon dioxide, and advantage has been taken of this reaction to generate free radicals not readily obtained by other methods.

\[ \text{COOR} \rightarrow \text{CO}_2 + \text{R} \]  \( \text{(2)} \)

A class of compounds which combines both of the above features is the esters of azodicarboxylic acid, \( \text{ROOCN} = \text{NCOOR} \). These compounds are easily prepared, are reddish, and decompose at temperatures above about 120°. They may be useful as potential thermal and photochemical sources of alkyl radicals, since by analogy with reactions 1 and 2 the following sequence of reactions might be expected:

\[ \text{ROOCN} = \text{NCOOR} \rightarrow \text{N}_2 + 2\text{COOR} \]  \( \text{(3)} \)

\[ \text{COOR} \rightarrow \text{CO}_2 + \text{R} \]  \( \text{(4)} \)

Although the use of these compounds in connection with the Diels–Alder reaction is well known, their decomposition appears not to have been examined. We have studied the thermal decomposition of dimethyl azodiformate in the gas phase and in dodecane solution.

Experimental Section

Materials. Dimethyl azodiformate was prepared by the method of Rodgman and Wright,\(^{6}\) a fraction boiling at 80.5° at 6.5 mm being collected. This was subjected to several bulb-to-bulb distillations on a vacuum line before being stored in a blackened bulb. Gas chromatographic analysis showed the sample to be pure.

Apparatus. In the gas-phase study, the azodiformate was condensed into a cylindrical Pyrex reaction vessel (volume 180 cm\(^3\)) equipped with a break-seal and sealed off under vacuum. The reaction vessel was then immersed in a thermostated oil bath capable of maintaining temperatures up to 200° to better than ±1°. The reaction was stopped by removing the vessel from the oil bath and plunging it into a bath at −80°.

The reaction vessel was then sealed onto a high-vacuum line and the break-seal was broken. The reaction products were expanded into an analytical train which was comprised of a liquid nitrogen trap, a gas buret, and a Madeed gauge. The products not condensable in liquid nitrogen were collected and measured in the gas buret before being analyzed mass spectrometrically. A second fraction was removed at −121° using a pentane–liquid nitrogen slush bath and was similarly analyzed.

In the liquid-phase study, the decomposition was investigated in dodecane with 10⁻² \( M \) solutions being used. The reaction vessels were cylindrical Pyrex tubes (volume ca. 5 cm\(^3\)) which could be filled with solution leaving only a small space above the liquid. The ampoules were sealed off and the runs and analysis were performed as described above.

A similar analytical procedure was used for the photolysis studies, the light source being the full beam of a Mazda ME/D250W medium-pressure mercury lamp.

Remarks and Discussion

Gas-Phase Decomposition. A series of runs were carried out at 162°. The noncondensable fraction contained no methane and consisted entirely of nitrogen. Analysis of the fraction volatile at -121° showed it to contain only about 3% ethane, the remainder being carbon dioxide with traces of the azodiformate ester. A typical product analysis yielded the following values (in micromoles): N₂, 205; CO₂, 1.94; and C₂H₆, 0.06; i.e., N₂/CO₂ = 1.06 and 2C₂H₆/CO₂ = 0.66.

\[
CH₃OOCN\rightleftharpoons NCOOCH₃ \rightarrow N₂ + 2CH₃OOCCI
\] (5)

\[
CH₃OOCCI \rightarrow CH₄ + CO₂
\] (6)

Decomposition of the ester according to reactions 5 and 6 would require that the ratios N₂/CO₂ and ΣCH₄/CO₂ would have the values 0.5 and 1, respectively. We interpret the divergence of our experimental values from these predicted values to indicate that only about half of the methoxy carbonyl radicals generated in reaction 5 decompose. It appears that approximately 6% of the methyl radicals produced in the decarboxylation reaction are accounted for by the reaction

\[
2CH₃ \rightarrow C₂H₆
\] (7)

Methyl radicals have been shown to react very readily with azomethane⁹ by addition to form trimethyl hydrazine and tetramethyl hydrazine. Our experimental results suggest that they may also react very readily with the azodiformate. It is likely also that some of the unaccounted for methoxy carbonyl radicals have reacted by addition to the N=N bond. Conjugation with the two carbonyl groups appears to have the effect of enhancing the rate of radical addition to the double bond. This reaction must be fast, since it is clearly competitive with reaction 6 and very much faster than the hydrogen atom abstraction reaction

\[
CH₃₋ + CH₃OOCN = NCOOCH₃
\] (8)

because no methane is detected.

Rate constants (based on nitrogen evolution) were measured for reaction 5 at 162°. The results of five repeat determinations yielded a value \( k_5 = (6.4 \pm 0.9) \times 10^{-6} \text{ sec}^{-1} \), the error limit representing the average deviation of these runs. If a preexponential factor of \( 10^{14} \text{ sec}^{-1} \) is assumed, this rate corresponds to an activation energy for reaction 5 of about 38 kcal mol⁻¹. This may be compared with a value of 34.6 kcal mol⁻¹ for the activation energy reported¹⁰ for the decomposition of tetramethyldiazene, i.e., where R = (CH₃)₂N₉ in reaction 1.

Decomposition in Dodecane Solution. When \( 10^{-2} \text{ M} \) solutions in dodecane were decomposed thermally at temperatures in the range 120–170° or photochemically at a lower temperature, a colorless sticky polymerlike solid was produced which went brown on standing. The bright red solution was rapidly bleached, suggesting complete consumption of the azodiformate, although the maximum yield of nitrogen indicated that only about 7% of the azodiformate had decomposed.

Analysis of the polymerlike solid showed it to contain C, 44.1%; N, 12.8%; H, 6.4%; and O, 30.8% (by difference). This corresponds to a formula of C₅H₁₃NO₁₃, the molecular weight of which is 466, in reasonable agreement with the molecular weight of 500 ± 20 determined directly using a vapor pressure osmometer.

We consider that these results may be interpreted in terms of a ready addition of the radicals produced in reactions 5 and 6 to the azo linkage. The resulting radical then undergoes an isomerization reaction

\[
CH₃OOCN(R)COOCH₃ \rightarrow CH₃OC(O)\rightleftharpoons NN(R)COOCH₃
\]

This radical in turn reacts by addition to the azodiformate and in this manner a repeating unit (ON-(COOCH₃)N=C(OCH₃)₋)ₙ is built up. Our molecular weight determination suggests a value of about 3 or 4 for \( n \). This ready addition reaction rapidly consumes all of the azodiformate and this explains why the solution is bleached, although actual thermal decomposition of dimethyl azodiformate based upon nitrogen evolution only accounts for a relatively small consumption of the ester.

It is clear that because of this complication the decomposition of azodiformate esters is not likely to be of use as a free-radical source.

Acknowledgment. We thank Professor Peter Gray for several helpful discussions.

Intramolecular Elimination Reactions in the Photolysis of Fluoroaldehydes

Sir: Recently, perfluoroalkyl radicals have been generated by the photolysis of various fluoroaldehydes, and data have been obtained for the abstraction of the aldehydic hydrogen atom by the radical

$$\text{R}_t + \text{HCOR}_t \rightarrow \text{R}_t\text{H} + \text{COR}_t$$

The aldehyde has also been used as a radical source to investigate the removal of hydrogen from various substrate molecules, i.e.

$$\text{R}_t + \text{RH} \rightarrow \text{R}_t\text{H} + \text{R}$$

This technique is satisfactory if there is no other source of $\text{R}_t\text{H}$ in the reaction system.

In a study of the photolysis of $\text{C}_3\text{F}_5\text{COCl}_{\text{F}_7}$-$\text{HCOC}_2\text{F}_5$, mixtures it became apparent that although the fluoroform formation could be adequately accounted for by the reactions

$$\text{CF}_4 + \text{HCOC}_2\text{F}_5 \rightarrow \text{CF}_3\text{H} + \text{COC}_2\text{F}_5$$
$$2\text{CF}_3 \rightarrow \text{C}_2\text{F}_6$$

the pentafluoroethane formation was not similarly expressed by the reactions

$$\text{C}_2\text{F}_5 + \text{HCOC}_2\text{F}_5 \rightarrow \text{C}_2\text{F}_5\text{H} + \text{COC}_2\text{F}_5$$
$$2\text{C}_2\text{F}_5 \rightarrow \text{C}_4\text{F}_{10}$$

Our evidence for this conclusion was that although a plot of the ratio $R_{\text{CF}_3\text{H}}/R_{\text{C}_2\text{F}_5}$ vs. aldehyde concentration gave, within experimental error, zero intercept, a corresponding plot for $R_{\text{C}_2\text{F}_5\text{H}}/R_{\text{C}_2\text{F}_5}^{1/2}$ yielded a markedly positive intercept. Analysis of the data published for the $\text{HCOC}_2\text{F}_5$ system yielded essentially the same conclusion.

When cyclopropanecarboxaldehyde is photolyzed, its decomposition has been shown to involve production of free radicals and also the formation of propylene by an intramolecular elimination reaction (8).

$$\text{HCO} \rightarrow \overset{7}{\text{HCO} + \text{H}}$$
$$\overset{8}{\text{CO} + \text{CH}_2=\text{CH} - \text{CH}_2}$$

It seemed likely that such an intramolecular elimination reaction was also contributing to pentafluoroethane formation when the fluoroaldehyde was photolyzed; i.e., the primary processes were

$$\text{HCOC}_2\text{F}_5 \rightarrow \text{HCO} + \text{C}_2\text{F}_5$$
$$\overset{10}{\text{CO} + \text{C}_2\text{F}_5\text{H}}$$

We have photolyzed under similar conditions the aldehyde alone and also aldehyde-nitric oxide mixtures. In the latter cases perfluorobutane formation was completely inhibited although extensive pentafluoroethane formation occurred, the yield decreasing by only $\sim 75\%$ at 400°K compared with the experiments performed in the absence of the inhibitor. We therefore conclude that reaction 10 contributes substantially to pentafluoroethane formation. The fact that only such a relatively small degree of $\text{C}_2\text{F}_5\text{H}$ inhibition was observed, particularly with regard to the fact that, in the unscavenged experiments there will be substantial contributions to the $\text{C}_2\text{F}_5$ radical concentration by the decarbonylation of the $\text{COC}_2\text{F}_5$ radical produced in reaction 5, suggests that photodecomposition of the aldehyde by reactions 9 and 10 must be comparable.

Similar examination of the photolyses of $\text{HOCOF}_3$ and $\text{HCOCF}_3$ showed that the following intramolecular elimination reactions occur appreciably in these systems.

$$\text{HCOCF}_3 \rightarrow \text{CO} + \text{CF}_3\text{H}$$
$$\text{HCOCF}_3\text{F} \rightarrow \text{CO} + \text{C}_2\text{F}_5\text{H}$$

We therefore conclude that fluoroaldehydes are not suitable for use as photochemical sources of fluoroalkyl radicals in connection with hydrogen atom abstraction reactions and that the kinetic data reported for such reactions are likely to be significantly in error.


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Reactions of Radicals Containing Fluorine

Part 4.—Reactions of Trifluoromethyl Radicals with Fluoroaldehydes

By E. R. Morris and J. C. J. Thynne

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Received 15th May, 1968

The reactions of trifluoromethyl radicals, generated by the photolysis of hexafluoroacetone, with the aldehydes HCOCF₃, HCOC₂F₅ and HCOC₃F₇ have been studied and the following Arrhenius parameters determined:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log A (mole⁻¹ cm³ sec⁻¹)</th>
<th>E (kcal mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃⁺HCOCF₃ → CF₃H + COCF₃</td>
<td>11·95 ± 0·10</td>
<td>8·8 ± 0·2</td>
</tr>
<tr>
<td>CF₃⁺HCOC₂F₅ → CF₃H + COC₂F₅</td>
<td>11·12 ± 0·09</td>
<td>6·7 ± 0·2</td>
</tr>
<tr>
<td>CF₃⁺HCOC₃F₇ → CF₃H + COC₃F₇</td>
<td>11·09 ± 0·11</td>
<td>6·6 ± 0·2</td>
</tr>
</tbody>
</table>

The rate of hydrogen atom abstraction from the fluoroaldehydes at 164°C is independent of the size of the fluoroalkyl group. Direct photolysis of the aldehydes HCOCF₃, HCOC₂F₅ and HCOC₃F₇ is complicated by the intramolecular elimination reactions:

\[ \text{hv} \quad \text{HCOR} \xrightarrow{} \text{R} + \text{CO} \]

where R = CF₃, C₂F₅ and C₃F₇.

A value of 1·95, which is independent of temperature, has been obtained for the cross-combination of CF₃ and C₂F₅ radicals.

For a wide variety of aldehydes, the velocity constants for the hydrogen atom abstraction reactions (1) and (2) are similar and not influenced by the size of the alkyl group R.⁠¹⁻³

1. \[ \text{CH₃} + \text{HCOR} \xrightarrow{} \text{CH₄} + \text{COR} \]
2. \[ \text{R} + \text{HCOR} \xrightarrow{} \text{RH} + \text{COR} \]

Replacement of the alkyl groups by fluoroalkyl groups, R_f, appears to have little effect on the rate of hydrogen atom abstraction when the attacking radical is methyl⁣⁴:

3. \[ \text{CH₃} + \text{HCOR}_f \xrightarrow{} \text{CH₄} + \text{COR}_f \]

The situation where the radical abstracting hydrogen from the fluoroaldehyde is a fluoroalkyl radical (reaction (4)) is less clear-cut and there appears to be a divergence between the results reported where R_f is CF₃⁤ and where R_f is C₂F₅ or C₃F₇,⁶ the latter radicals being the more reactive in removing hydrogen atoms from the appropriate aldehyde:

4. \[ \text{R}_f + \text{HCOR}_f \xrightarrow{} \text{R}_f \text{H} + \text{COR}_f \]

This difference might be real and ascribed to the nature of the attacking radical and the strength of the R_f—H bond formed, though D (CF₃—H) is stronger than in the other molecules,⁷ or to the influence of the fluoroalkyl group on the reactivity of the aldehydic hydrogen atom. It might also reflect some complication in the photolysis of pentafluoropropionaldehyde or heptafluorobutyraldehyde leading to an additional source of R_fH in these decompositions.

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A study of the reaction of the same fluoroalkyl radical with a variety of fluoroaldehydes should give information regarding some of these problems, and accordingly we have investigated the reaction of trifluoromethyl radicals with the aldehydes, CF₃CHO, C₂F₅CHO and C₃F₇CHO. Our data also enable the cross-combination ratio for CF₃ and C₂F₅ radicals to be evaluated and information to be deduced regarding hydrogen-atom abstraction from the parent aldehydes by the C₂F₅ and C₃F₇ radicals.

**EXPERIMENTAL**

**APPARATUS AND PROCEDURE**

The apparatus used has been described. Trifluoromethyl radicals were generated by the photolysis of hexafluoroacetone at λ > 3000 Å. Because of the spectral overlap of the absorption bands of the ketone and the aldehydes used, there was also simultaneous photolysis of the aldehydes. Except for CF₃CHO, photodecomposition of the aldehydes does not influence the formation of CF₃H and C₂F₆. With CF₃CHO, the reaction was complicated by the formation of CF₃H by a direct intramolecular elimination reaction. We therefore used mixtures rich in ketone in order to obtain a relatively high CF₃ radical concentration so as to minimize the intramolecular contribution to CF₃H formation. Mixtures of aldehyde and ketone were made up in a 500 mL bulb before being expanded into the reaction cell. After reaction, the products were trapped at liquid-nitrogen temperature and the non-condensable gases removed by pumping. The remainder of the reaction products were then analyzed gas chromatographically, our technique permitting analysis of the compounds, CF₃H, C₂F₅H, C₂F₆, C₃F₇H, C₄F₈ and C₄F₁₀. Samples of C₂F₅H, C₃F₈ and C₄F₁₀ were obtained by prolonged photolysis of the appropriate aldehyde or mixture of aldehydes and collecting the compounds as they were eluted from the gas chromatograph.

**MATERIALS**

Hexafluoroacetone was prepared by dehydration of the sesquihydrate (Koch-Light). The product contained small quantities of CO₂, C₂F₆ and CF₃H as impurities; these were removed by prolonged pumping at -130°C. The aldehydes were prepared from their hydrates as described previously.

**RESULTS AND DISCUSSION**

**REACTIONS OF CF₃ WITH HCOR**

When trifluoromethyl radicals are produced in the presence of a fluoroaldehyde, fluoroform and hexafluoroethane are produced. Their formation may be accounted for by the reactions:

\[ \text{CF}_3 + \text{HCOR} \rightarrow \text{CF}_3\text{H} + \text{COR} \]  
\[ 2\text{CF}_3 \rightarrow \text{C}_2\text{F}_6. \]

Ayscough has measured the rate constant for the combination of trifluoromethyl radicals obtaining the value \( k_6 \) (mole\(^{-1}\) cm\(^3\) sec\(^{-1}\)) = 10\(^{13.34}\). We use this value in the results discussed below.

\[ R_f = \text{C}_2\text{F}_5 \]

The reaction products analyzed for in this system were CF₃H, C₂F₅H, C₂F₆, C₃F₇ and C₄F₁₀. Our analytical data are shown in table 1. Their formation is discussed in terms of the following reactions:

\[ \text{CF}_3 + \text{HCOC}_2\text{F}_5 \rightarrow \text{CF}_3\text{H} + \text{COC}_2\text{F}_5 \]

\[ \text{COC}_2\text{F}_5 \rightarrow \text{CO} + \text{C}_2\text{F}_5 \]
Table 1.—Hydrogen-atom abstraction from \( \text{C}_2\text{F}_5\text{CHO} \) by \( \text{CF}_3 \) radicals

| \( T^\circ \text{K} \) | time (sec) | \( [\text{ald}] \) | \( [\text{ket}] \) | \( \text{CF}_3\text{H} \) | \( \text{C}_2\text{F}_6 \) | \( \text{C}_2\text{F}_2\text{H} \) | \( \text{C}_3\text{F}_8 \) | \( \text{C}_4\text{F}_{10} \) | \( k_1/k_2 \) | \( \phi \) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 555-6 | 900 | -250 | -384 | 63-1 | 3-62 | 101 | 39-0 | 35-2 | 67-7 | 1-82 |
| 526-3 | 200 | -522 | -519 | 106 | 18-1 | 193 | 66-2 | 65-5 | 47-6 | 1-92 |
| 500-0 | 600 | -300 | -352 | 37-8 | 14-3 | 53-9 | 39-4 | 26-8 | 33-3 | 2-02 |
| 500-0 | 200 | -500 | -536 | 72-2 | 22-8 | 109 | 63-3 | 51-5 | 30-3 | 1-85 |
| 500-0 | 100 | -111 | -680 | 36-6 | 91-2 | 16-9 | 57-0 | 8-6 | 34-6 | 2-04 |
| 476-2 | 450 | -287 | -644 | 35-4 | 30-7 | 40-2 | 48-2 | 20-7 | 22-3 | 1-91 |
| 454-5 | 450 | -688 | -696 | 53-7 | 26-8 | 93-4 | 70-4 | 46-2 | 15-1 | 2-01 |
| 434-8 | 450 | -399 | -876 | 23-6 | 30-9 | 35-9 | 22-7 | 10-6 | 1-90 |
| 400-0 | 600 | -676 | -730 | 11-5 | 9-82 | 59-5 | 31-8 | 31-6 | 5-44 | 1-81 |
| 400-0 | 200 | -157 | 2-36 | 9-98 | 79-4 | 11-6 | 46-7 | 7-2 | 1-95 |
| 400-0 | 600 | -850 | -587 | 3-78 | 52-1 | 5-3 | 28-0 | 4-2 | 6-17 | 1-90 |
| 400-0 | 200 | -160 | -989 | 8-53 | 90-4 | 11-6 | 51-5 | 7-1 | 5-61 | 2-04 |
| 400-0 | 600 | -093 | 1-61 | 6-11 | 72-4 | 8-2 | 38-5 | 4-9 | 7-72 | 2-04 |
| 400-0 | 200 | -459 | 1-40 | 17-6 | 26-7 | 37-8 | 48-4 | 20-8 | 7-45 | 2-06 |
| 400-0 | 450 | -555 | 1-74 | 17-3 | 28-1 | 32-6 | 49-9 | 23-8 | 5-54 | 1-92 |
| 384-6 | 450 | -724 | -701 | 8-68 | 8-63 | 51-2 | 34-6 | 34-4 | 4-08 | 2-01 |
| 370-4 | 450 | -553 | 1-18 | 8-21 | 22-8 | 31-9 | 49-3 | 26-1 | 3-11 | 2-03 |
| 357-1 | 450 | 1-19 | 1-13 | 5-41 | 4-47 | 60-0 | 25-8 | 41-1 | 2-15 | 1-91 |

ket = \( \text{CF}_3\text{COCF}_3 \); aldehyde and ketone concentrations in \( 10^6 \) mole \( \text{cm}^{-3} \); rates of formation of products in \( 10^{12} \) mole \( \text{cm}^{-3} \) \( \text{sec}^{-1} \);
\[ \phi = \frac{R_{\text{C}_2\text{F}_6}}{R_{\text{CF}_3\text{H}}R_{\text{C}_3\text{F}_8}} \]
TRIFLUOROMETHYL RADICAL REACTIONS

\[ \text{C}_2\text{F}_5 + \text{HCOC}_2\text{F}_5 \rightarrow \text{C}_2\text{F}_5\text{H} + \text{COC}_2\text{F}_5 \]

\[ \text{CF}_3 + \text{C}_2\text{F}_5 \rightarrow \text{C}_3\text{F}_9 \]

\[ 2\text{C}_2\text{F}_5 \rightarrow \text{C}_4\text{F}_{10} \]

\[ \text{HCOC}_2\text{F}_5 + h\nu \rightarrow \text{HCO} + \text{C}_2\text{F}_5 \]

\[ \rightarrow \text{C}_2\text{F}_5\text{H} + \text{CO} \]

\[ \text{CF}_3 + \text{HCO} \rightarrow \text{CF}_3\text{H} + \text{CO} \]

\[ \text{C}_2\text{F}_5 + \text{HCO} \rightarrow \text{C}_2\text{F}_5\text{H} + \text{CO}. \]

If reactions (7) and (9) are solely responsible for the formation of CF\(_3\)H and C\(_2\)F\(_5\)H respectively, then the following rate relationships apply:

\[ \frac{R_{\text{CF}_3\text{H}}}{[\text{ald}]} = \frac{k_7}{k_8} \text{ and } \frac{R_{\text{C}_2\text{F}_5\text{H}}}{[\text{ald}]} = \frac{k_9}{k_{11}}. \]

where \( R_X \) is the rate of formation of \( X \) and [ald] refers to the mean aldehyde concentration.

When \( R_{\text{CF}_3\text{H}}/R_{\text{CF}_2\text{F}_5} \) is plotted against the aldehyde concentration a linear plot is obtained which, within experimental error, passes through the origin. At 400°K e.g., the intercept for such a plot was 0.17 ± 0.22 × 10\(^{-6}\) and hence it may be concluded that there is no further source of CF\(_3\)H. Our data for reaction (7) are expressed by

\[ \log k_7 \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11.12 \pm 0.09 \text{ -(6700 ± 200)/2.303 RT}. \]

The error limits quoted in this paper are the standard deviations obtained by a least-mean-squares computer treatment.

C\(_2\)F\(_5\) radicals are generated in this system by direct photolysis of the aldehyde and also by decarbonylation of the perfluoroacyl radical produced in the hydrogen-atom abstraction reactions. These radicals react by hydrogen atom removal from the aldehyde and also by auto-combination yielding C\(_2\)F\(_5\)H and C\(_4\)F\(_{10}\) respectively. A plot of the ratio \( R_{\text{CF}_3\text{H}}/R_{\text{CF}_2\text{F}_5} \) against aldehyde concentration reveals a markedly positive intercept, a value of 2.4 ± 0.6 × 10\(^{-6}\) (mole\(^3\) cm\(^{-3}\) sec\(^{-1}\)) being obtained for the experiments at 400°K. When the data of Pritchard et al.\(^6\) for the experiments performed at 300°K are plotted in this manner, the dependence of their rate ratio on aldehyde concentration is small, a large intercept (≈ 8 × 10\(^{-6}\) mole\(^4\) cm\(^{-4}\) sec\(^{-4}\)) being obtained.

These observations suggest that there is a further contribution to the pentafluoroethane formation which probably involves photodecomposition of the aldehyde. Formyl radicals are produced by photolysis of the aldehyde (reaction (12)) and hence the disproportionation reaction (15) may contribute to C\(_2\)F\(_5\)H formation. We regard this reaction as unlikely since if it occurred then it would probably be paralleled by the cross-disproportionation of CF\(_3\) and HCO radicals (14). Our zero-intercept for the aldehyde dependence of the ratio \( R_{\text{CF}_3\text{H}}/R_{\text{CF}_2\text{F}_5} \) indicates that no such reaction is occurring. We therefore conclude that (15) does not contribute to C\(_2\)F\(_5\)H formation in our experiments.

The intramolecular elimination of propylene in the photolysis of cyclopropane-carboxaldehyde has been established.\(^{10}\) It seemed possible that photolysis of the pentafluoropropionaldehyde also involved an intramolecular elimination reaction such as (13) producing pentafluoroethane. To examine this possibility, we photolyzed...
the aldehyde alone and also in the presence of sufficient nitric oxide to scavenge free radicals. We found complete inhibition of perfluorobutane formation but extensive formation of pentfluoroethane in the experiments with added nitric oxide. In similar experiments at 400°K, the rate of formation of C₂F₅H was reduced from $7.5 \times 10^{-12}$ to $2.5 \times 10^{-12}$ (mole cm⁻³ sec⁻¹) by the addition of nitric oxide. These observations suggest that there is extensive formation of C₂F₅H by reaction (13) and indicate that the Arrhenius parameters deduced by Pritchard et al.⁶ are likely to be significantly in error.

We are therefore unable to calculate a value for $k_9$ from our data. A value may be estimated, however, by correcting for the intramolecular contribution to C₂F₅H (obtained from the inhibited experiments) and then calculating $k_9/k_{11}$ in the usual manner. By this means we have estimated a value of $8.6 \pm 2.8$ (mole⁻¹ cm² sec⁻¹) for the rate constant ratio at 400°K. The corresponding value for $k_7/k_8$ is $6.0 \pm 1.1$, from which we may tentatively conclude that reactions (7) and (9) take place at very similar rates.

$$R_f = C_3F_7$$

The condensable reaction products observed in this reaction were CF₃H, C₂F₆, C₃F₇H and C₄F₁₀, but only the first two were consistently analyzed for. The reactions involved are:

16. CF₃ + HCOC₃F₇ → CF₃H + COC₃F₇
17. COC₃F₇ → CO + C₃F₇
18. C₃F₇ + HCOC₃F₇ → C₂F₅H + COC₃F₇;
19. CF₃ + C₃F₇ → C₄F₁₀
20. HCOC₃F₇ + hv → HCO + C₃F₇
21. → C₃F₇H + CO.

The rate relation,

$$R_{CF_3H}/R_{C_2F_6}[ald] = k_{16}/k_8,$$

may be obtained. The ratio $R_{CF_3H}/R_{C_2F_6}$ shows a linear dependence on aldehyde concentration the line passing through the origin within our experimental error, so that reaction (16) is the sole source of CF₃H formation. Our data are shown in table 2 and the velocity constant for (16) may be expressed by the equation:

$$\log k_{16} \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11.09 \pm 0.11 - (6570 \pm 220)/2.303 RT.$$

In view of the intramolecular reaction established above for pentafluoropropion-aldehyde, the photolysis of the heptafluoroaldehyde in the presence of nitric oxide was investigated. Considerable formation of heptafluoropropane in the inhibited system indicated that it was probable that reaction (21) was occurring. Accordingly, to study its formation by reaction (18) alone was not feasible in this work. The participation of reaction (21) in the direct photolysis of the aldehyde suggests that the reported⁶ Arrhenius parameters for this reaction are incorrect.

$$R_f = CF_3$$

When the ketone and aldehyde are photolyzed together, CF₃H and C₂F₆ are produced as reaction products. The results reported above for photolysis of
TRIFLUOROMETHYL RADICAL REACTIONS

HCOCF$_3$ and HCOC$_3$F$_7$ suggested that an intramolecular reaction leading to fluoroform formation might also occur for HCOCF$_3$. Accordingly, we photolyzed the aldehyde alone and in the presence of nitric oxide and found that, although C$_2$F$_6$ formation was eliminated in the inhibited experiments, substantial yields of CF$_3$H were obtained, indicating the occurrence of the reaction,

$$\text{HCOCF}_3 + h\nu \rightarrow \text{CF}_3\text{H} + \text{CO}.$$  

We have attempted to reduce the contribution of reaction (22) to CF$_3$H formation in this reaction system by using mixtures rich in ketone. Accordingly we attribute the major contribution to the fluoroform formation to be reaction (23):

$$\text{CF}_3 + \text{HCOCF}_3 \rightarrow \text{CF}_3\text{H} + \text{COCF}_3.$$  

The rate relation is

$$R_{\text{CF}_3\text{H}}/R_{\text{C}_2\text{F}_6}[\text{ald}] = k_{23}/k_{22}.$$  

**Table 2.—Hydrogen-atom abstraction from C$_3$F$_7$CHO by CF$_3$ radicals**

<table>
<thead>
<tr>
<th>$T^\circ$K</th>
<th>$t$ (sec)</th>
<th>[ald]</th>
<th>[ket]</th>
<th>rates of formation</th>
<th>$k_{16}/k_{8}^\frac{1}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>555-6</td>
<td>200</td>
<td>-500</td>
<td>-991</td>
<td>162</td>
<td>30-4</td>
</tr>
<tr>
<td>555-6</td>
<td>200</td>
<td>-326</td>
<td>1-20</td>
<td>136</td>
<td>37-3</td>
</tr>
<tr>
<td>526-3</td>
<td>200</td>
<td>-463</td>
<td>-918</td>
<td>126</td>
<td>25-5</td>
</tr>
<tr>
<td>526-3</td>
<td>200</td>
<td>-170</td>
<td>2-11</td>
<td>97-0</td>
<td>148</td>
</tr>
<tr>
<td>476-2</td>
<td>200</td>
<td>-269</td>
<td>3-33</td>
<td>92-1</td>
<td>245</td>
</tr>
<tr>
<td>434-8</td>
<td>300</td>
<td>-593</td>
<td>2-19</td>
<td>70-1</td>
<td>103</td>
</tr>
<tr>
<td>400-0</td>
<td>900</td>
<td>-915</td>
<td>1-81</td>
<td>36-2</td>
<td>41-6</td>
</tr>
<tr>
<td>400-0</td>
<td>100</td>
<td>-737</td>
<td>1-46</td>
<td>31-9</td>
<td>43-1</td>
</tr>
<tr>
<td>400-0</td>
<td>450</td>
<td>-391</td>
<td>1-44</td>
<td>19-7</td>
<td>73-4</td>
</tr>
<tr>
<td>400-0</td>
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<td>-890</td>
<td>-859</td>
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<td>12-2</td>
</tr>
<tr>
<td>400-0</td>
<td>150</td>
<td>1-44</td>
<td>1-39</td>
<td>37-6</td>
<td>11-7</td>
</tr>
</tbody>
</table>

ket = CF$_3$COCF$_3$; aldehyde and ketone concentrations in $10^{6}$ mole cm$^{-3}$; rates of formation of products in $10^{12}$ mole cm$^{-3}$ sec$^{-1}$.

Our results are shown in table 3. When the aldehyde was photolyzed alone a plot of the ratio $R_{\text{CF}_3\text{H}}/R_{\text{C}_2\text{F}_6}$ against aldehyde concentration showed a marked positive intercept (~20 x $10^{-6}$ mole$^3$ cm$^{-3}$ sec$^{-1}$). When the results for the mixed system are plotted, the intercept is close to zero (1 x $10^{-6}$) suggesting that most of the fluoroform formation is accounted for by reaction (23). We have used these data to calculate the velocity constant $k_{23}$:

$$\log k_{23} \text{ (mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11-96 \pm 0-10 - (8780 \pm 220)/2-303 RT.$$  

We have not included the results for experiments carried out at 400 and 416-7°K in our least-squares calculation since these data indicated curvature of the Arrhenius plot in this temperature region, presumably because at such temperatures contributions from reaction (22) to the total fluoroform yield are significant.

Our data are in reasonable accord with those obtained from a direct photolysis of the aldehyde by Dodd and Smith who report $A_{23} = 11-73$ and $E_{23} = 8-4$ kcal mole$^{-1}$, and who also observed curvature of the Arrhenius plot below 425°K.
COMPARISON OF RATE CONSTANTS

In table 4 we have compared the kinetic data available for reactions of types (1), (3) and (4). From the results of the present work, variation of the fluoroalkyl group has little effect on reactivity of the aldehydic hydrogen atom since the rate constants for reactions (7), (16) and (23) are almost identical at 164°C, a conclusion which is in accord with results reported \(^1,\,^4\) for reactions (1) and (3). The Arrhenius

<table>
<thead>
<tr>
<th>&lt;table 3.—Hydrogen-atom abstraction from CF₃CHO by CF₃ radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>rates of formation</td>
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<td></td>
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</tr>
<tr>
<td>555.6</td>
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<td>555.6</td>
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<td>400.0</td>
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<td>400.0</td>
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<td>400.0</td>
</tr>
</tbody>
</table>

ket = CF₃COCF₃; aldehyde and ketone in 10⁶ mole cm⁻³; CF₃H and C₂F₆ in 10¹² mole cm⁻³ sec⁻¹.

log \(k\) = \(E\) / \(R\) T

<table>
<thead>
<tr>
<th>Table 4.—Arrhenius parameters and velocity constants at 164°C for hydrogen atom abstraction reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>reaction</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>CF₃ + CF₃CHO</td>
</tr>
<tr>
<td>CF₃ + C₂F₅CHO</td>
</tr>
<tr>
<td>CF₃ + C₃F₇CHO</td>
</tr>
<tr>
<td>CH₃ + CF₃CHO</td>
</tr>
<tr>
<td>CH₃ + C₂F₅CHO</td>
</tr>
<tr>
<td>CH₃ + C₃F₇CHO</td>
</tr>
<tr>
<td>CH₃ + CH₃CHO</td>
</tr>
<tr>
<td>CH₃ + C₂H₅CHO</td>
</tr>
<tr>
<td>CH₃ + C₂F₅CHO</td>
</tr>
<tr>
<td>CH₃O + CH₃OCHO</td>
</tr>
</tbody>
</table>

parameters for reactions (7) and (16) are similar but for trifluoroacetalddehyde the values are much higher, the difference being quite outside our experimental error. This difference of about 2 kcal mole⁻¹ in the activation energy requirements is unexpected and inexplicable since the rate constants in this region do not differ. The reactivity of the aldehydic hydrogen atom is slightly lower for the fluoroaldehydes indicating that fluoroalkyl groups have a slight deactivating effect on the hydrogen atom attached to the adjacent carbon atom.
Our "corrected" value for the rate constant for reaction (9) suggests that, as for alkyl radicals, the rate for the reaction \( R_2 + HCO \rightarrow R_2H + CO \) is likely to be similar to the analogous reaction involving CF\(_3\) radicals:

\[
X + HCO \rightarrow XH + COX
\]

In table 4 we have also included data for the reaction of methoxyl radicals with methyl formate,\(^{11}\) i.e., where \( X = OCH_3 \). Although there is little similarity in the Arrhenius parameters for the three systems where \( X = CH_3, CH_3O \) and CF\(_3\), the velocity constants are almost identical at 164°C. It would be of interest to obtain data for the reaction:

\[
(CH_3)N + HCON(CH_3)_2 \rightarrow (CH_3)_3N + CO(NH_3)_2,
\]

i.e., where \( X = N(CH_3)_2 \), to see if a comparable velocity constant was obtained or whether the similarity noted above is due primarily to the similarity of the H—C bond strength in the systems where \( X = CH_3, CH_3O \) and CF\(_3\).

**CROSS-COMBINATION OF CF\(_3\) AND C\(_2\)F\(_5\) RADICALS**

When hexafluoroacetone + pentafluoropropionaldehyde mixtures are photolyzed, CF\(_3\) and C\(_2\)F\(_5\) radicals are produced. These may react by auto- and cross-combination yielding C\(_2\)F\(_6\), C\(_4\)F\(_{10}\) and C\(_3\)F\(_8\). The following relation holds:

\[
R_{C_2F_6}/R_{C_4F_{10}}^+ = k_1/0.10(k_2^+)^{-1}(k_1^+)^{-1}.
\]

This rate ratio is the cross-combination ratio \( \phi \), and Kerr and Trotman-Dickenson\(^1, 12\) have shown that for many alkyl radicals it has the value of 2, expected on the basis of the simple collision theory. Our results for this ratio \( \phi \) are shown in column 11, table 2. The ratio is independent of temperature, within experimental error, and has the mean value 1.95. Gordon\(^13\) has reported a value of 2.08 for this ratio and, for CF\(_3\) and C\(_3\)F\(_7\) radicals, Pritchard et al.\(^14\) have obtained a value of 1.77.

We thank the Laporte Chemical Co., for financial support.

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PRELIMINARY COMMUNICATION

COMPARISON OF THE REACTIVITY OF TETRAMETHYLSILANE AND NEOPENTANE TOWARDS FREE RADICAL ATTACK

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(Received March 14th, 1969)

Recently, Chaudhry and Gowenlock\(^1\) have measured the Arrhenius parameters for the reaction of methyl radicals with a series of Group IV tetramethyils and concluded that the central atom affected the reactivity of the C—H bonds towards methyl radical attack.

We have studied the abstraction of hydrogen atoms from tetramethylsilane by methyl and trifluoromethyl radicals; comparison of our data with the analogous reactions for neopentane should yield information regarding (1) the effect of substitution of the central carbon atom by silicon upon the Arrhenius parameters for the reactions:

\[
\begin{align*}
\text{CH}_3 + (\text{CH}_3)_4 \text{X} & \rightarrow \text{CH}_4 + (\text{CH}_3)_3 \text{XCH}_2 \\
\text{CF}_3 + (\text{CH}_3)_4 \text{X} & \rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_3 \text{XCH}_2
\end{align*}
\]

and (2) the effect of the polar radical upon the C—H bond reactivity in these compounds.

Below we summarise the Arrhenius parameters and velocity constants at 164° (where 2.303 \(RT\) is 2000) for the neopentane and tetramethylsilane systems.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\log A) (mole(^{-1}) cm(^3) sec(^{-1}))</th>
<th>(E) (kcal mole(^{-1}))</th>
<th>(\log k) (164°) (mole(^{-1}) cm(^3) sec(^{-1}))</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3+(\text{CH}_3)_4 \text{Si})</td>
<td>11.5 ± 0.2</td>
<td>10.3 ± 0.4</td>
<td>6.35</td>
<td>this work</td>
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<tr>
<td>(\text{CH}_3+(\text{CH}_3)_4 \text{C})</td>
<td>11.3</td>
<td>10.0</td>
<td>6.3</td>
<td>2</td>
</tr>
<tr>
<td>(\text{CF}_3+(\text{CH}_3)_4 \text{Si})</td>
<td>12.0 ± 0.1</td>
<td>7.6 ± 0.2</td>
<td>8.2</td>
<td>this work</td>
</tr>
<tr>
<td>(\text{CF}_3+(\text{CH}_3)_4 \text{C})</td>
<td>11.8</td>
<td>7.6</td>
<td>8.0</td>
<td>3</td>
</tr>
</tbody>
</table>

It is apparent that, for attack by the same radical, the Arrhenius parameters and velocity constants are identical, within experimental error, for neopentane and tetramethylsilane. We therefore conclude that substitution of the central carbon atom by silicon has little effect upon the reactivity of the adjacent C—H bonds.

Comparison of the abstraction reactions of the methyl and trifluoromethyl radicals with the same substrate shows that the effect of the polar radical is to markedly increase the velocity constant, there being a pronounced lowering (~ 2.5 kcal mole\(^{-1}\)) of the activation energy requirements in both cases; this is in accord with results reported previously for hydrocarbon systems by Pritchard\(^4\).

REFERENCES


<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^1$H nmr, ppm (in CDCl$_3$)</th>
<th>$^1$C nmr, ppm (in CDCl$_3$)</th>
<th>$^1$H nmr, ppm (in CD$_2$Cl$_2$)</th>
<th>$^1$C nmr, ppm (in CD$_2$Cl$_2$)</th>
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</thead>
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<td>138.2, 141.8</td>
<td>1.0, 1.1</td>
<td>1.1</td>
<td>1.1</td>
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<tr>
<td>Grow alga 1</td>
<td>6.8, 7.1</td>
<td>138.3, 141.9</td>
<td>1.0, 1.2</td>
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