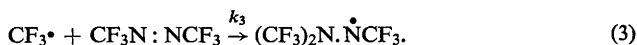


THE REACTIONS OF TRIFLUOROMETHYL RADICALS

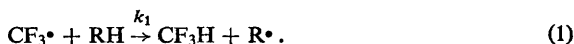
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AND A. F. TROTMAN-DICKENSON §

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(a) The photolysis of hexafluoroazomethane yields trifluoromethyl radicals which both combine (2) and add to the N : N bond (3) :



In the presence of a hydrogen-containing compound, RH, CF_3H is produced by (1) :



So many of the radicals add to the parent compound (3) that k_1 cannot be accurately compared with k_2 ; the rate of this addition is given by

$$k_3/k_2^{\frac{1}{2}} = 3.0 \times 10^3 \exp [-(3,500 \pm 200)/RT] \text{ mole}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}}$$

between -70° and 100°C .

(b) The rate constants k_1 for a number of compounds have been compared with k_5 ,



by measurement of the relative rates of production of CF_3H and CF_3D in a photolytic system containing RH, deuterium and hexafluoroazomethane. A_1 and E_1 have been determined from the Arrhenius equations. It is found that E_1 is in general 2 or 3 kcal/mole lower than the activation energy for the corresponding methyl radical reactions.

(c) The heat of the reaction $\text{CF}_3\cdot + \text{CH}_4 \rightarrow \text{CF}_3\text{H} + \text{CH}_3\cdot$ has been derived from the activation energies of the forward and reverse reactions, leading to the value

$$D(\text{CF}_3 - \text{H}) = D(\text{CH}_3 - \text{H}) - 0.5 \text{ kcal/mole}.$$

In recent years much work has been done to determine the Arrhenius parameters of reactions involving atoms and small free radicals. Most progress has been made in the determination of the rate constants of those reactions in which the atom or radical abstracts a hydrogen atom from a hydrogen-containing compound—usually a hydrocarbon. The reactions of methyl radicals¹ have been very fully investigated. Less is known about the reactions of chlorine,² hydrogen and bromine atoms and ethyl radicals.^{3,4} The ultimate object of much of this work has been to discover the factors determining the rates of reactions through the study of many series of similar reactions and the correlation of their rates with the thermodynamic and structural properties of the reactants. Particular interest attaches to the reactions of the trifluoromethyl radical because (as is shown in the present work) the $\text{CF}_3\text{—H}$ bond is almost the same strength as the $\text{CH}_3\text{—H}$ bond, though the $\text{CF}_3\cdot$ radical is probably much more electronegative than the $\text{CH}_3\cdot$ radical. Also, $\text{CF}_3\cdot$ has a much higher moment of inertia (and hence rotational entropy) than $\text{CH}_3\cdot$. Consequently, the entropy change occurring in the symmetrical dissociation of C_2F_6 is much greater than that which occurs when C_2H_6 dissociates, so that either the Arrhenius A factors for the two

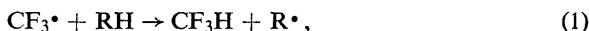
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dissociations or the two recombinations (or possibly both) must be very different. No direct evidence on this point has been obtained in the course of the present work, but it should be borne in mind when the A factors of $\text{CF}_3\cdot$ metathetical reactions are considered.

It might be expected that, by analogy with the reactions of methyl radicals, in the presence of a saturated hydrocarbon RH , trifluoromethyl radicals would undergo the two competing reactions



and



The rates of formation of CF_3H and C_2F_6 respectively would then be given by the two expressions:

$$R_{\text{CF}_3\text{H}} = d[\text{CF}_3\text{H}]/dt = k_1[\text{CF}_3\cdot][\text{RH}]$$

and

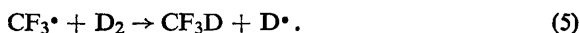
$$R_{\text{C}_2\text{F}_6} = d[\text{C}_2\text{F}_6]/dt = k_2[\text{CF}_3\cdot]^2,$$

whence

$$k_1/k_2^{\frac{1}{2}} = R_{\text{CF}_3\text{H}}/R_{\text{C}_2\text{F}_6}^{\frac{1}{2}}[\text{RH}].$$

The temperature coefficient of this rate ratio is the difference in activation energies $E_1 - \frac{1}{2}E_2$ and the pre-exponential factor is $A_1/A_2^{\frac{1}{2}}$. The results obtained in this research bear out this expectation.

Hexafluoroazomethane was chosen as a source of trifluoromethyl radicals, both because it is fairly simple to prepare and because its photolysis can be effected by visible (blue) light; thus the range of compounds RH is not restricted only to compounds which do not absorb in the near ultra-violet. First, it was necessary to investigate the photolysis of hexafluoroazomethane which is described in section (a); next, an attempt was made to determine $k_1/k_2^{\frac{1}{2}}$ by analysis for CF_3H and C_2F_6 formed during the photolysis of hydrocarbon + hexafluoroazomethane mixtures, but because of inherent difficulties, this approach was abandoned in favour of a method yielding relative rate constants by the comparison of the rate of a series of reactions of type 1 with reaction (5),



This part of the work is described in section (b), followed by the determination of the $\text{CF}_3\text{—H}$ bond strength in section (c).

EXPERIMENTAL

MATERIALS.—Hexafluoroazomethane was prepared by heating ICN and IF_5 in a steel bomb at 130 to 140°C .⁵ The contents of the bomb were then pumped into a trap containing solid KOH at liquid nitrogen temperature where any HF and most of the free iodine produced in the reaction were absorbed; the product could then be handled conveniently in all glass apparatus. The major impurity was stated by Ruff and Willenberg⁵ to be *bis*trifluoromethylamine $(\text{CF}_3)_2\text{NH}$ (which probably arises from the presence of HF in the IF_5); it was removed by shaking the gas first with dilute hydrochloric acid, which decomposes the impurity to HF , HOCN and CO_2 , and then with dilute sodium hydroxide solution to remove these acid products and any residual iodine. The product was dried over P_2O_5 and stored in the dark at liquid nitrogen temperature.

Mass spectrographic analysis showed this product to be essentially $\text{CF}_3\text{N}:\text{NCF}_3$, containing some CF_3I , SiF_4 and small amounts of hydrocarbons up to and including C_5 . Photolysis of this material at 25°C yielded a mixture of C_2F_6 and CF_3H containing nearly 40 % CF_3H , showing that the hydrogen-containing impurities were extremely susceptible to $\text{CF}_3\cdot$ radical attack. Further purification was effected by repeated fractional distillation at temperatures in the range -120 to -155° until photolysis yielded a C_2F_6 fraction containing only 1.3 % CF_3H . This material was considered to be sufficiently pure for the purposes of the present investigation; its molecular weight was found to be 168 (after correction for deviation from the gas laws) and the only impurity detectable in the mass spectrum was a trace of CF_3I .

Hexafluoroazomethane is a faintly greenish gas; b.p. -31.6° ; Ruff and Willenberg gave the vapour pressure as

$$\log_{10} P \text{ (in mm)} = (-1196/T) + 7.832,$$

and our measurements are in excellent agreement with this equation in the temperature range -35 to -80° . They stated that the gas decomposes in the presence of mercury giving $N_2 + C_2F_6$, but we have not confirmed this observation; the gas is stable in the dark, even in the presence of mercury, but is slowly decomposed by daylight. The gas exhibits a very intense absorption in the infra-red spectral region; the principal absorption lines and their relative intensities are given in table 1. The very weak triplet near 2800 cm^{-1} could be due to C—H vibrations, but their general disposition suggests that it is more likely to be a combination band (we are indebted to Dr. G. D. Meakins for discussion on this point); furthermore, a number of detailed searches of the mass spectrum have failed to reveal the presence of any hydrogen atoms in the product.

TABLE 1.—INFRA-RED ABSORPTION SPECTRUM OF HEXAFLUOROAZOMETHANE

(cm^{-1})	intensity	(cm^{-1})	intensity	(cm^{-1})	intensity
2950	v.w.	1860	w.	1084	s.
2850	v.w.	1825	v.w.	1079	s.
2782	w.	1773	w.	1072	s.
2470	m.	1667	v.w.	1034	m.
2250	v.w.	1581	m.	1025	m.
2202	m.	1562	m.	973	w.
2140	m.	1532	w.	949	m.
2072	m.	1458	m.	878	m.
2022	m.	1404	s.	744	m.
1955	w.	1274	v.s.	739	m.
1915	v.w.	1210	v.s.	733	m.

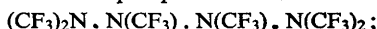
Note.—Spectra were observed with pressures of 280, 14 and 1 mm Hg in a 10 cm absorption cell: v.w. indicates that the absorption can only be detected at 280 mm, whereas v.s. indicates 50-80 % absorption at 1 mm pressure; w., m., and s. denote intermediate intensities.

Deuterium was prepared by electrolysis of a saturated solution of Na_2SO_4 in 99.7 % D_2O , and was freed from O_2 and D_2O by passing through a quartz tube containing boiling sodium; mass spectrometer analyses yielded $D_2 = 96.5\%$, $HD = 3.5\%$. Hydrogen was obtained from a cylinder and was purified using a palladium thimble. The aliphatic hydrocarbons used were standard samples supplied by the Chemical Research Laboratory, Teddington; acetone and benzene were of A.R. grade and the toluene was a pyrolyzed sample. Hexadeuteroacetone was kindly given to us by the National Research Council, Ottawa.

APPARATUS AND PROCEDURE.—Most of the experiments were carried out using a 300 ml quartz reaction vessel which was isolated from the main vacuum system by a mercury cut-off. This vessel was enclosed in an electric furnace, whose temperature could be controlled to $\pm 2^{\circ}$ in the range 30 to 350° , and was irradiated with light from a high-pressure mercury lamp for periods of from 3 to 24 h. After irradiation, the contents of the reaction vessel were pumped out and separated by low-temperature fractional distillation; the volume of each fraction was measured before being removed from the apparatus for mass spectrometric analysis.

(a) THE PHOTOLYSIS OF HEXAFLUOROAZOMETHANE

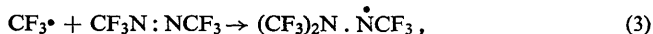
The photolysis of hexafluoroazomethane at room temperature and 5 cm pressure leads to the production of nitrogen, hexafluoroethane, a trace of fluoroform (as mentioned above) and a liquid product having a vapour pressure of 20-30 cm at room temperature (20°). This was shown by mass spectrographic analysis to be $(CF_3)_2N \cdot N(CF_3)_2$; presumably it is formed by the addition of CF_3^{\bullet} radicals to the N:N double bond in hexafluoroazomethane. The relative volumes of products in one run at room temperature were N_2 9.8, C_2F_6 1.9, CF_3H 0.025 and $(CF_3)_4N_2$ 7.8; the almost exact material balance shows that all the CF_3^{\bullet} radicals are accounted for and that about 80 % of them are lost by addition to the parent compound. At higher temperatures the material balance is not maintained and the liquid product contains the compound



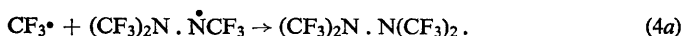
our identification of these liquid products is based on mass spectrometric evidence, and is confirmed in a paper by Dacey and Young ⁶ which appeared after this work was completed. No evidence was found for the formation of any CF₄ up to the highest temperatures used (350°); however, above about 150°, small amounts of CO₂ and SiF₄ were produced by the attack of CF₃• radicals on the quartz. A similar attack was found by Ayscough and Emeléus ⁷ in the pyrolysis of As(CF₃)₃ and Sb(CF₃)₃, but Sieger and Calvert ⁸ did not find it in their photolysis experiments with trifluoroacetone.

The kinetics of the addition reaction were studied in a subsidiary apparatus: samples of hexafluoroazomethane were sealed in a 170 ml Pyrex cylinder which was placed in a thermostatted air-space whose temperature could be maintained constant to $\pm 1^\circ\text{C}$ in the range from room temperature to -70°C . After illumination with light from a mercury vapour lamp (for a period of time sufficient to decompose about 5 % of the azo-compound), the reaction vessel was re-attached to the main apparatus, the seal broken, and the contents analysed.

In those experiments performed at or below room temperature, the only products were N₂, C₂F₆ and (CF₃)₂N·N(CF₃)₂; we have assumed that the production of perfluorotetramethylhydrazine takes place by



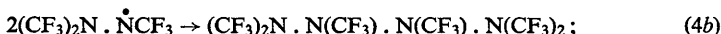
which is rate-determining, followed by the fast reaction



Thus, the rate constant for the addition is given by

$$k_3/k_2^{\frac{1}{2}} = R_{(\text{CF}_3)_2\text{N}\cdot\text{N}(\text{CF}_3)_2} / R_{\text{C}_2\text{F}_6}^{\frac{1}{2}} [\text{CF}_3\text{N}:\text{NCF}_3].$$

The Arrhenius plot of these results is given in fig. 1. A further point, obtained from experiments carried out (in the main apparatus) at 100° C also lies on this straight line; at this temperature some perfluorohexamethyltetrazine was formed, presumably by the reaction



from a knowledge of the drop in pressure during the reaction and the total quantity of the liquid product, the extent of reaction (3) was obtained leading to the highest temperature point shown in fig. 1. Fitting these results to the Arrhenius equation leads to the expression

$$k_3/k_2^{\frac{1}{2}} = 3.0 \times 10^3 \exp [-(3,500 \pm 200)/RT] \text{ moles}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}}.$$

(b) THE REACTION OF CF₃• RADICALS WITH HYDROGEN-CONTAINING COMPOUNDS

In some earlier experiments, an attempt was made to compare the rates of reactions (1) and (2) by photolyzing hexafluoroazomethane in the presence of hydrocarbons and comparing the rates of formation of CF₃H and C₂F₆. However, the extreme ease with which radicals were removed by reaction (3) so reduced the static concentration of CF₃• radicals that only minute amounts of C₂F₆ were formed, and it was only by extending the temperature range over at least 200° C that even approximate data about the relative activation energies of reactions (1) and (2) could be obtained.⁹ It was therefore decided to investigate only the relative reactivities of a series of compounds RH towards CF₃• radical attack; this was done by photolyzing about 2 cm of hexafluoroazomethane in the presence of about 10 cm of D₂ and sufficient RH to produce a reasonable ratio of CF₃D to CF₃H for analytical purposes. Thus the rates of a whole series of reactions were related to the rate of the reaction,



from a knowledge only of the ratio of RH and D₂ present, and the ratio of CF₃H to CF₃D produced. The latter ratio was determined mass-spectrometrically from the relative abundances of the CF₂H⁺ and CF₂D⁺ peaks, allowing for ¹³C contributions and making the assumption that the cracking patterns and sensitivities of the two molecules are similar. (Should they differ slightly, this will reflect itself in the relative frequency factors, but the relative activation energies will remain unchanged.) A detailed set of results for the reaction with H₂ + D₂ mixtures is given in table 2 and fig. 2, and in fig. 3 the Arrhenius plots for a series of RH + D₂ mixtures are given. We considered it the purpose of this work to explore the whole field of CF₃• radical reactivity, and in consequence,

most of the Arrhenius plots are based on four or five points; the whole of this data is summarized in table 3 (together with some less reliable data on *isobutane*, benzene and toluene). For the purposes of calculating absolute values of $E_1 - \frac{1}{2}E_2$, we have chosen Ayscough, Polanyi and Steacie's result¹² for $\text{CF}_3^\bullet + \text{C}_2\text{H}_6$ as a standard and all the values given in table 3, with the exception of those for methane, are related to this determination; the corresponding rate factors for CH_3^\bullet radical reactions are also given in table 3 for comparison.

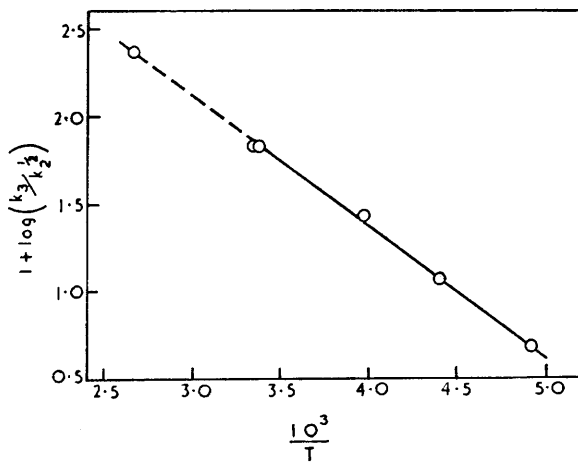


FIG. 1.

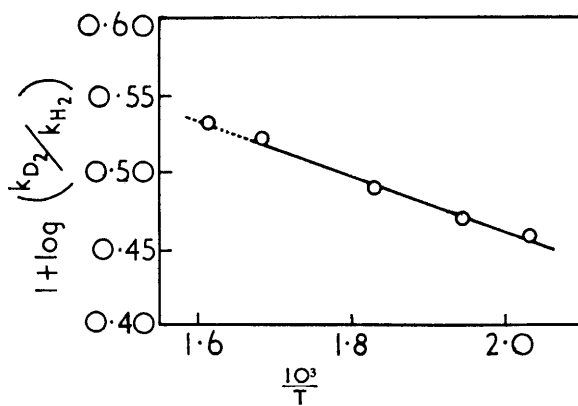


FIG. 2.

TABLE 2.—THE REACTION OF CF_3^\bullet RADICALS WITH HYDROGEN + DEUTERIUM MIXTURES

temp. °C	time (min)	pressure D_2 (cm)	pressure H_2 (cm)	$[\text{CF}_3\text{D}]/[\text{CF}_3\text{H}]$	k_5/k_1
219	300	12.74	3.23	1.135	0.287
241	270	9.53	2.59	1.087	0.295
273	210	8.92	4.41	0.624	0.309
320	60	8.95	6.14	0.486	0.334
344	10	9.35	4.01	0.750	0.321
346	10	7.45	4.96	0.387	0.362

$$k_5/k_1 = \frac{d[\text{CF}_3\text{D}]/dt}{d[\text{CF}_3\text{H}]/dt} \frac{[\text{H}_2]}{[\text{D}_2]} = 0.69 \exp [-(860 \pm 80)/RT].$$

These and other results have been corrected for the fact that a proportion of the CF_3H arises from HD originally present in the D_2 ; the extent of this correction was estimated from a consideration of the results of Whittle and Steacie¹⁰ on the reactions $\text{CH}_3^\bullet + \text{HD}$ and $\text{CD}_3^\bullet + \text{HD}$. Also, in those runs carried out above 320°C , difficulty was encountered because hexafluoroazomethane decomposes ($\rightarrow \text{N}_2 + 2\text{CF}_3^\bullet$) thermally (at 300°C the rate is equivalent to 10 % decomposition in 1 h¹¹): consequently, at 345°C an average had to be taken over two runs carried out using complementary mixing procedures (i.e. injection into reaction vessel in the order [substrate + H_2 + D_2] and [substrate + D_2 + H_2]).

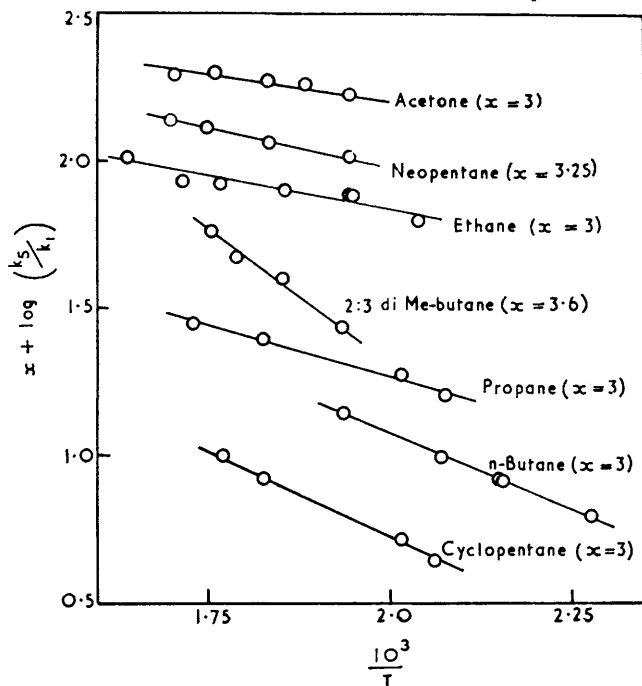


FIG. 3.

TABLE 3.—COMPARISON OF CF_3^\bullet AND CH_3^\bullet RADICAL H-ABSTRACTION REACTIONS

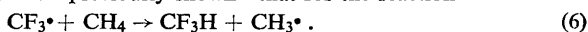
RH	CF_3^\bullet radical reactions				CH_3^\bullet radical reactions ^a	
	$E_5 - E_1$ kcal/mole	A_5/A_1	$E_1 - \frac{1}{2}E_2$ kcal/mole	$A_1/A_2^{\frac{1}{2}} \times 10^{-4}$ mole $^{-\frac{1}{2}}$ cm $^{\frac{3}{2}}$ sec $^{-\frac{1}{2}}$	$E_1 - \frac{1}{2}E_2$ kcal/mole	$A_1/A_2^{\frac{1}{2}} \times 10^{-4}$ mole $^{-\frac{1}{2}}$ cm $^{\frac{3}{2}}$ sec $^{-\frac{1}{2}}$
deuterium	—	—	9.7	5.8	11.8	(12.9)
hydrogen	0.86 ± 0.08	0.69	8.8	8.4	10.0	(21.8)
methane	—	—	10.3^b	9.7^b	~ 13	—
ethane	2.20 ± 0.50	0.62	7.5^b	9.4^b	10.4	2.8
neopentane	2.10 ± 0.20	0.47	7.6	12	10.0	3.0
propane	3.5 ± 0.5	0.60	6.2	9.7	—	—
n-butane	4.40 ± 0.10	0.97	5.3	6.0	8.3	1.6
cyclopentane	5.0 ± 0.2	0.81	4.7	7.2	8.3	3.6
isobutane	~ 6.7	(8.0)	(3.0)	(0.73)	7.6	1.5
2:3-diMebutane	8.0 ± 1.0	16.7	1.7	0.35	6.9	1.0
acetone	1.7 ± 0.5	0.85	8.0	6.8	9.7	6.0
benzene	~ 2	(1.0)	(7.7)	(5.8)	9.2	0.37
toluene	3.7 ± 1.0	1.30	6.0	4.5	8.3	2.1

^a methyl radical values from Trotman-Dickenson, ref. (1) and Whittle and Steacie, ref. (10).

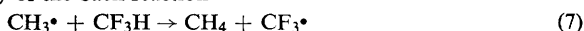
^b from Ayscough, Polanyi and Steacie, ref. (12).

(c) THE C—H DISSOCIATION ENERGY IN FLUOROFORM

It is impossible to understand the factors governing the rates of these CF_3^\bullet radical reactions without a knowledge of their thermochemistry. Before this investigation was undertaken, virtually nothing was known with any certainty about the strengths of bonds formed by the CF_3 —group, and in consequence, we have measured $D(\text{CF}_3\text{—H})$ by the classical kinetic method. We had previously shown⁹ that for the reaction



$E_6 - \frac{1}{2}E_2$ was in the range 9.5 ± 2 kcal/mole, and this has been confirmed by Ayscough, Polanyi and Steacie¹² who derived a more precise figure of 10.3 ± 0.5 kcal from experiments in which hexafluoroacetone was photolyzed in the presence of methane; a knowledge of the activation energy of the back reaction



is then sufficient to give $D(\text{CF}_3\text{—H})$ by the relationship,

$$D(\text{CH}_3\text{—H}) - D(\text{CF}_3\text{—H}) = E_6 - E_7.$$

Furthermore, it is now reasonably well established that the isotopic substitution of the

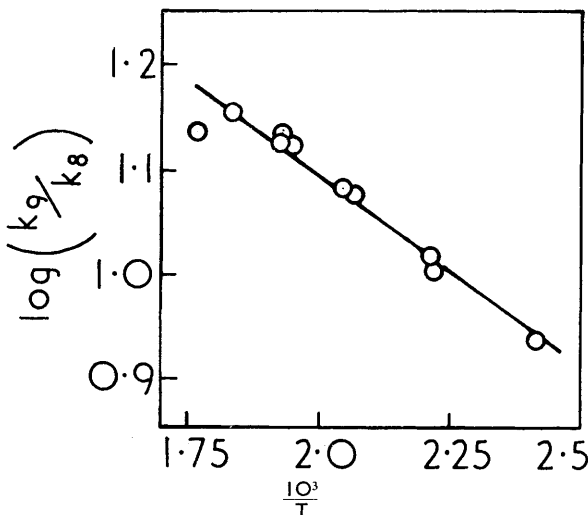


FIG. 4.

three hydrogen atoms in the methyl radical makes very little difference to its reactivity,^{10, 13} so that we may identify E_7 with E_8 , the activation energy of the process,



which is much more easily measured experimentally.

Mixtures of about 5 cm of 95 % acetone- d_6 and some 5-20 cm of fluoroform were photolyzed at temperatures in the range 140-290° C; the fraction of the products volatile at -195°C (i.e. CO , CD_4 and CD_3H) was separated off, and the ratio of $[\text{CD}_3\text{H}]/[\text{CD}_4]$ was determined mass-spectrometrically. In addition to reaction (8), the CD_3^\bullet radicals can undergo the reactions



Thus the rate of reaction (8) can be related to the known rate of reaction (9) by the expression

$$\frac{k_9}{k_8} = \frac{d[\text{CD}_4]/dt}{d[\text{CD}_3\text{H}]/dt} \frac{[\text{CF}_3\text{H}]}{[\text{CD}_3\text{COCOD}_3]};$$

the results of ten experiments are listed in table 4 and the Arrhenius plot is shown in fig. 4, leading to the relation $k_9/k_8 = 75 \exp [-(1800 \pm 150)/RT]$ (the error quoted being the maximum deviation of the Arrhenius plot). The activation energy of reaction (9) is known relative to that of reaction (10) from work on the photolysis of acetone- d_6 by Whittle

and Steacie,¹⁰ and their value of $E_9 - \frac{1}{2}E_{10} = 11.6$ kcal/mole has been confirmed indirectly by McNesby and Gordon.¹³ Using these results, we have

$$E_6 = (10.3 + \frac{1}{2}E_2) \text{ and } E_7 = E_8 = (11.6 + \frac{1}{2}E_{10} - 1.8),$$

whence $D(\text{CF}_3\text{—H}) = D(\text{CH}_3\text{—H}) - 10.3 - \frac{1}{2}E_2 + 11.6 + \frac{1}{2}E_{10} - 1.8$.

$$= D(\text{CH}_3\text{—H}) - \frac{1}{2}E_2 + \frac{1}{2}E_{10} - 0.5 \text{ kcal/mole.}$$

E_{10} is known to be zero, but there have been numerous suggestions that because of the highly polar nature of the C—F bond, there may be a potential barrier to the combination of two CF_3^\bullet radicals and that E_2 may differ considerably from zero (see, e.g., Sieger and Calvert, ref. (8)); such arguments are fallacious as it can be shown that a potential barrier to combination will arise only when there is a change in multiplicity of one or more of the atoms in the system; in reaction (2) as in reaction (10), the multiplicities of all centres remain unchanged throughout the course of the combination process. Thus, if we assume that $D(\text{CH}_3\text{—H}) = 102.5 \pm 1$,¹⁴ we have $D(\text{CF}_3\text{—H}) = 102.0 \pm 2$ kcal/mole.

TABLE 4.—THE PHOTOLYSIS OF ACETONE- d_6 IN THE PRESENCE OF FLUOROFORM

temp. °C	$[\text{CF}_3\text{H}]/[\text{acetone-}d_6]$	$[\text{CD}_3\text{H}]/[\text{CD}_4]$ (corrected)*	k_9/k_8
142	1.091	0.127	8.56
178	1.433	0.143	10.02
180	0.903	0.087	10.41
211	3.123	0.262	11.92
216	0.589	0.049	12.12
244.5	3.517	0.258	13.63
245.5	1.803	0.133	13.56
246	0.639	0.048	13.43
271.5	0.760	0.053	14.31
292.5	3.462	0.253	13.68

* This column has been corrected for the proportion of CD_3H formed from the H atom impurity in the heavy acetone; this correction was approximately constant over the whole temperature range and amounted to 0.071 ± 0.006 .

DISCUSSION

The competitive method which we have developed in this work provides a simple and accurate means of determining the rate factors for a whole series of reactions, $\text{CF}_3^\bullet + \text{RH} \rightarrow \text{CF}_3\text{H} + \text{R}^\bullet$, once the relevant data are known for one such reaction of this type. The only difficulty arises in the preparation of deuterated substandards of sufficient isotopic purity. For example, we have not been able to study the methane reaction by this method because methane is so unreactive that as much CF_3H would be formed from reaction with the HD impurity in the D_2 as from reaction with the methane itself. The correction to be applied would then be too large for the results to be of any value. Some difficulty was experienced also at the other end of the reactivity scale (i.e. with 2:3-dimethylbutane and with *isobutane*) because they are so much more reactive than D_2 : this difficulty can, however, be overcome in principle by the use of a deuterated substandard of intermediate reactivity, for example, C_2D_6 ; we have not performed any experiments of this kind.

The results obtained for the competition between H_2 and D_2 (see table 2 and fig. 2) are of particular interest. The activation energy for CF_3^\bullet radical attack on D_2 is greater than for H_2 by an amount which is approximately half of the difference in zero-point energy between these molecules, and the ratio of the frequency factors is 0.69, which is almost exactly equal to the ratio of the relative collision numbers (i.e., $2^{-\frac{1}{2}}$) for the two reactions. In view of this result, it seems unlikely that the activation energies for the corresponding CH_3^\bullet radical reactions could differ by 1.8 kcal (cf. the values of 11.8 and 10.0 given by Whittle and Steacie¹⁰); note, however, that Whittle and Steacie also found 11.1 kcal for the activation energy for $\text{CD}_3^\bullet + \text{H}_2$ which seems more reasonable in comparison

with the activation energy for $\text{CH}_3^\bullet + \text{D}_2$. It can be seen by a comparison of columns 4 and 6 of table 3 that in general the reactions of CF_3^\bullet radicals have activation energies about 2 or 3 kcal less than the corresponding CH_3^\bullet radical reactions. (This, too, appears to be true for the addition to the N:N double bond, if we compare the value of 3.5 kcal obtained in this work for



with that of 6.5 obtained by Jones and Steacie¹⁵ for $\text{CH}_3^\bullet + \text{CH}_3\text{N}:\text{NCH}_3$). On the other hand, the frequency factor ratios A_1/A_2^\ddagger for the two sets of reactions are in general very similar but it is difficult at this stage to comment further on this similarity because we cannot quote with any certainty the relative frequency factors for the combination reactions of the two radicals.

The fact that the activation energies for CF_3^\bullet radical reactions are lower than those for CH_3^\bullet radicals is, however, readily understandable in terms of the idea that activation energies and electronegativities are related.² It so happens that reaction (6) is virtually thermoneutral, making possible a direct comparison with three other reactions in which a hydrogen atom is abstracted from the methane molecule. In table 5, the relevant data on these reactions, all of which are thermo-neutral to within the experimental error, are presented.

TABLE 5

reaction	activation energy, E (kcal/mole)	Mulliken electronegativity, χ (eV)
$\text{Cl}^\bullet + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3^\bullet$	3.9	9.5
$\text{H}^\bullet + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3^\bullet$	10.0	7.2
$\text{CF}_3^\bullet + \text{CH}_4 \rightarrow \text{CF}_3\text{H} + \text{CH}_3^\bullet$	10.3	> 6
$\text{CH}_3^\bullet + \text{CH}_4 \rightarrow \text{CH}_4 + \text{CH}_3^\bullet$	~ 13	~ 6

It is not suggested that all four reactions form one series (i.e. one cannot use the values of E to derive a value for χ for the CF_3^\bullet radical): however, it is clear that the increase in χ on going from H^\bullet to Cl^\bullet is accompanied by a substantial decrease in E ; likewise, on going from CH_3^\bullet to CF_3^\bullet (which is known to be much more electronegative than the methyl radical¹⁶) there is again a significant drop in the value of E . This effect will be equally operative throughout the whole series of CF_3^\bullet reactions studied, so that they all must have activation energies slightly lower than the corresponding CH_3^\bullet radical reactions.

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