960

THE REACTIONS OF TRIFLUOROMETHYL RADICALS WITH HYDROGEN ISOTOPES *

BY P. B. AYSCOUGH † AND J. C. POLANYI ‡

Division of Pure Chemistry, National Research Council, Ottawa James Forrestal Research Center, Princeton University, New Jersey

Received 24th January, 1956

The photolytic decomposition of hexafluoroacetone has been used to produce trifluoromethyl radicals for a study of their reactions with hydrogen isotopes. Activation energies for the four reactions: $CF_3 + H_2 \rightarrow CF_3H$, $CF_3 + HD \rightarrow CF_3D$, $CF_3 + HD \rightarrow CF_3D$ and $CF_3 + D_2 \rightarrow CF_3D$ were found to be, respectively, 9.5 ± 0.7 , 10.5 ± 1.5 , 10.2 ± 1.5 and 10.2 ± 0.7 kcal mole⁻¹. The results are discussed in detail in terms of the collision theory and the absolute theory of reaction rates. Evidence is adduced for a progressive decline in pre-exponential factor down the series of reactions: $H + H_2$, $CH_3 + H_2$, $CF_3 + H_2$.

⁺ National Research Council Post-Doctorate Fellow, 1953-55. Present address: School of Chemistry, The University, Leeds 2.

^{*} Contribution no. 3985 from the Division of Pure Chemistry, National Research Council of Canada, Ottawa. This research was supported in part by the United States Air Force under contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

[†] National Research Council Post-Doctorate Fellow, 1952-54.

P. B. AYSCOUGH AND J. C. POLANYI

Recently, through the work of Majury and Steacie¹ and Whittle and Steacie,² the rate constants of the four reactions between methyl radicals and hydrogen isotopes, and also the four reactions between trideuteromethyl and hydrogen isotopes, have become known. In a theoretical discussion of these reactions by one of us ³ a model was suggested according to which the energy of activation could be shown to vary by only a small amount within these series of isotopic reactions. In accordance with this result it was found that the observed differences in rate constant could be largely accounted for by changes in the entropy of activation, that is to say, in the calculated pre-exponential factor.

The present work was undertaken to extend the experimental data to the four isotopic reactions: $CF_3 + H_2 \rightarrow CF_3H$, $CF_3 + HD \rightarrow CF_3H$, $CF_3 + HD \rightarrow CF_3D$, $CF_3 + D_2 \rightarrow CF_3D$, and to see to what extent the relative rates could once again be accounted for in terms of changing entropy of activation.

As yet, published work on the hydrogen abstraction reactions of trifluoromethyl includes investigations of its reactions with methane, ethane and higher hydrocarbons by Steacie and collaborators 4, 5 and by Pritchard, Pritchard and Trotman-Dickenson 6 and its reactions with trifluoroacetone by Sieger and Calvert.⁷ All these workers agree that the reactions of trifluoromethyl proceed with an activation energy 2-3 kcal mole⁻¹ less than that for the analogous reactions with methyl radicals.

EXPERIMENTAL

The apparatus was essentially the same as that used by Steacie and collaborators ⁴ for the photolysis of hexafluoroacetone in the presence of methane. In the present work however, the whole volume of the cell was illuminated. In most experiments standard filter combinations were used in order to confine the incident radiation to the 3130 Å region. In others, the potassium hydrogen phthalate filter was removed in order to pass light of wavelength 3025 Å also. This effectively doubled the intensity without causing any change in the rate constant ratio.

Hexafluoroacetone was prepared by the permanganate oxidation of perfluoroisobutene.⁸ Samples of cylinder hydrogen and deuterium were passed through a heated palladium thimble directly into the reaction vessel, a portion being analysed mass-spectrometrically before each run. Average analyses were, for hydrogen, 99.5 % H₂, and for deuterium, 97.5 % D₂. An equilibrium mixture of deuterium hydride, hydrogen and deuterium was prepared by heating approximately equal volumes of hydrogen and deuterium in a silica vessel for 48 h at 600° C. The resulting mixture was found, by mass-spectrometric analysis, to contain approximately 28 % H₂, 21 % D₂ and 51 % HD. Slight variations in composition occurred as samples were passed through the palladium thimble.

The experiments were generally allowed to proceed to about 5 % conversion and the products separated by distillation in the vacuum system, using two Ward stills in series. Carbon monoxide and hydrogen were removed together and oxidized in a copper oxide furnace to carbon dioxide and water. Hexafluoroethane, fluoroform and trifluorodeuteromethane were taken off in a second fraction and analysed mass-spectrometrically, assuming equal sensitivity for the CF_2H^+ and CF_2D^+ peaks. When only hexafluoroethane and fluoroform were present some analyses were made using infra-red spectrophotometry.⁹ The results were identical with those obtained by mass-spectrometry.

Rate constants were calculated assuming a reaction volume of 190 ml. Activation energies for the hydrogen and deuterium reactions were obtained directly from the Arrhenius plots.

RESULTS AND DISCUSSION

Hexafluoroacetone produces trifluoromethyl radicals when irradiated by light of wavelength 3130 Å and these radicals can abstract hydrogen from hydrocarbons.^{4, 5} When a mixture of hexafluoroacetone and hydrogen is photolyzed fluoroform is produced, indicating the abstraction of one hydrogen atom. Similarly, trifluorodeuteromethane is found when deuterium is used and a mixture of fluoroform and trifluorodeuteromethane in the presence of deuterium hydride.

These reactions may be represented as follows:

$$CF_3COCF_3 + hv \rightarrow 2CF_3 + CO$$
 (1)

$$2CF_3 \rightarrow C_2F_6 \tag{2}$$

$$CF_3 + H_2 \rightarrow CF_3H + H$$
 (3)

$$CF_3 + HD \rightarrow CF_3H + D$$
 (4)

$$CF_3 + HD \rightarrow CF_3D + H$$
 (5)

$$CF_3 + D_2 \rightarrow CF_3D + D.$$
 (6)

Fluoroform and trifluorodeuteromethane could also be formed by reactions (7) and (8):

$$CF_3 + H \rightarrow CF_3H$$
 (7)

$$CF_3 + D \rightarrow CF_3D.$$
 (8)

We must determine the importance of reactions (7) and (8) if we are to be able to estimate k_3 , etc. Considering the possible fate of the hydrogen and deuterium atoms formed by reactions (3) to (6), we find that, in addition to reactions (7) and (8) they may recombine in the presence of a third body, as represented by reactions (9) to (11):

$$\mathbf{H} + \mathbf{H} + \mathbf{M} \to \mathbf{H}_2 + \mathbf{M} \tag{9}$$

$$\mathbf{D} + \mathbf{D} + \mathbf{M} \to \mathbf{D}_2 + \mathbf{M} \tag{10}$$

$$H + D + M \rightarrow HD + M.$$
(11)

It is also possible, theoretically, that the hydrogen atoms may abstract either a fluorine atom or a trifluoromethyl group from the substrate :

$$H + CF_3COCF_3 \rightarrow HF + CF_2COCF_3 \tag{12}$$

$$H + CF_3COCF_3 \rightarrow CF_3H + CF_3 + CO.$$
(13)

However, no trace of hydrogen fluoride or any of the products of its reaction with silica (e.g. silicon tetrafluoride) could be found by mass-spectrometric analysis of the products, and it seems that hydrogen atoms are no more able to break the carbon-fluorine bond than are trifluoromethyl radicals.⁴, ⁷, ¹⁰ Reaction (13) seems no more likely since this would start a chain reaction. No indication of a chain reaction was found over a tenfold variation in light intensity. (It should be noted that in the photolysis of acetone in the presence of hydrogen it was considered, see ref. (2), that most of the hydrogen atoms disappeared by a reaction analogous to (12), namely,

$$H + CH_3COCH_3 \rightarrow H_2 + CH_2COCH_3$$
.

This could not, however, be proved directly.)

We are left, therefore, with reactions (7) to (11) as the principal means of removal of hydrogen and deuterium atoms. Calculations based on the material balance are of no assistance in determining the reaction path since the small changes in hydrogen or deuterium concentration cannot be measured with sufficient accuracy to decide between recombination and reaction with trifluoromethyl radicals.

Theoretical considerations do not help appreciably to clarify the mechanism. It is known that trifluoromethyl radicals, like methyl radicals, recombine at almost every collision ¹¹ and they also react very rapidly with molecular hydrogen. Hydrogen atoms recombine only in the presence of a third-body which can remove the excess energy, and reactions between hydrogen atoms and hydrogen molecules,

P. B. AYSCOUGH AND J. C. POLANYI

etc., do not alter the overall concentration. It would appear then that the stationary hydrogen atom concentration may be much greater than the concentration of trifluoromethyl radicals even if reactions (7) and (8) do take place (since these remove one of each). Reactions (9) to (11) will, therefore, be considerably favoured on concentration grounds if third-body restrictions on reactions (7) and (8) are comparable with those on reactions (9) to (11). Majury and Steacie ¹² suggested that the reaction of methyl with hydrogen required a third-body and it seems likely that the restrictions on the reaction of trifluoromethyl radicals

TABLE	1

temp. °K	time (sec)	$\begin{array}{c} \text{CF}_3\text{COCF}_3\\ \text{moles/cm}^3\\ \times 10^7 \end{array}$	H_2 moles/cm ³ × 10 ⁷	со	products C_2F_6 moles/sec × 1	CF3H 010	I $k_3/k_2^{\frac{1}{2}}$ cm ^{$\frac{3}{2}$} mole	II
332	5100	5.12	30.1	20.7	18.5	1.52	0.0426	0.0852
349.5	9000	4.77	23.7	5.82	5.14	0.963	0.0626	0.131
349.5	10800	4.54	22.5	7.20	6.27	1.455	0.0939	0.188
349.5	8100	4.77	43.7	4.82	3.59	1.507	0.0662	0.132
360	3600	10.9	24.2	42.3	39.1	5.68	0.136	0.272
372	3030	11.3	23.8	54·1	47.1	8.79	0.196	0.391
391	3300	10.25	20.3	51·0	45.4	12-0	0.338	0.675
407·5	6600	9.68	19.25	25.6	20.3	13.6	0.572	1.148
408	16800	12.5	11.2	1.42	0.72	1.55	0.590	1.180
419.5	2970	9.73	9.95	53.7	43·0	17.4	0.970	1.94
450	4800	8.89	8.35	25.7	15.2	17.7	1.97	3.94
458	7200	9.00	8.82	32.8	15.3	18.9	1.99	3.97

with hydrogen atoms will be similar. We therefore consider that reactions (9) to (11) are favoured on concentration grounds and that to a large extent hydrogen atoms recombine rather than react with trifluoromethyl radicals. We shall, however, calculate the results on the basis of the two extreme cases, called mechanism I and mechanism II. Mechanism I for the hydrogen reaction consists of reactions (1), (2), (3) and (7), and mechanism II consists of reactions (1), (2), (3) and (7). The results are presented in table 1. It can be shown that for mechanism I

$$k_3/k_2^{\frac{1}{2}} = \frac{\text{rate CF}_3H}{2(\text{rate C}_2F_6)^{\frac{1}{2}}[H_2]},$$

where rate CF₃H is the rate of formation of CF₃H, etc.; and for mechanism II

$$k_{3}/k_{2^{\frac{1}{2}}} = \frac{\text{rate CF}_{3}H}{(\text{rate C}_{2}F_{6})^{\frac{1}{2}}[H_{2}]}.$$

Similarly for the reaction with deuterium for mechanism I (reactions (1), (2), (4) and (8))

$$k_4/k_2^{\frac{1}{2}} = \frac{\text{rate CF}_3\text{D}}{2(\text{rate C}_2\text{F}_6)^{\frac{1}{2}}[\text{D}_2]},$$

and for mechanism II (reactions (1), (2) (4) and (10)

$$k_4/k_2^{\frac{1}{2}} = \frac{\text{rate CF}_3\text{D}}{(\text{rate C}_2\text{F}_6)^{\frac{1}{2}}[\text{D}_2]}.$$

Values are listed in table 2.

These expressions enable us to calculate the upper and lower limits of k_3 and k_4 , the ratio of the limiting values being 2:1 for either k_3 or k_4 .

 $\begin{aligned} R_2 &= R_4 \\ k_6/k_2^{\frac{1}{2}} \end{aligned}$

 $-\frac{1}{2} \sec^{-\frac{1}{2}}$ 0.0509

0.0817

0.159

0.248

0.496

II $\frac{1}{4/k_2^{\frac{1}{2}}}$ sec ^{$-\frac{1}{2}$}	I $k_4/k_2^{\frac{1}{2}}$ $\mathrm{cm}^{\frac{3}{2}}$ mole ⁻	CF3D	products C_2F_6 ples/sec × 10 ¹⁰	co _{mo}	$\begin{array}{c} \mathbf{D_2}\\ \mathrm{moles/cm^3}\\ imes 10^7 \end{array}$	CF_3COCF_3 moles/cm ³ $\times 10^7$	time (sec)	°K
0377	0.0178	0.490	14.2	15.6	26.2	10.18	2790	359
0643	0.0321	0.585	10.9	1 6 •6	20.0	7.05	2400	374
149	0.0744	1.15	20.7	21.3	12.3	10.22	2112	397
·208	0.104	1.49	16.6	17.1	12.8	9.84	2400	407 ·5
387	0.194	2.08	18-1	20.7	9·1 8	9.55	2100	430
670	0.335	3.66	19.6	21.0	8.97	9.44	2400	447.5
·639	0.320	3.50	19.6	21.3	8·99	8.22	2490	458
055	0.529	4.83	14.8	19-9	8.61	8.51	2100	469
03 06 14 20 38 67 63 05	0.0178 0.0321 0.0744 0.104 0.104 0.335 0.320 0.529	0·490 0·585 1·15 1·49 2·08 3·66 3·50 4·83	14·2 10·9 20·7 16·6 18·1 19·6 19·6 14·8	15.6 16.6 21.3 17.1 20.7 21.0 21.3 19.9	26-2 20-0 12-3 12-8 9-18 8-97 8-99 8-61	10-18 7-05 10-22 9-84 9-55 9-44 8-22 8-51	2790 2400 2112 2400 2100 2400 2490 2490 2100	359 374 397 407·5 430 447·5 458 469

TABLE 2

The case of deuterium hydride is more complicated since we have to consider all the reactions (1) to (11). We do not, however, have to consider the change in relative concentration of the isotopes from the metathetical reactions such as

 $H + HD \rightarrow H_2 + D$

since the amount of conversion was only about 5 % and we started with an equilibrium mixture.

The two limiting mechanisms give results as follows :

for mechanism I (reactions (1) to (8))

$$\frac{k_5 + k_6}{k_2^{\frac{1}{4}}} = \left(\frac{\text{rate } CF_3H}{(\text{rate } C_2F_6)^{\frac{1}{4}}[H_2]} - \frac{2k_3}{k_2^{\frac{1}{4}}}\right) \frac{[H_2]}{[HD]} = R_1,$$

$$\frac{k_5 + k_6}{k_2^{\frac{1}{4}}} = \left(\frac{\text{rate } CF_3D}{(\text{rate } C_2F_6)^{\frac{1}{2}}[D_2]} - \frac{2k_4}{k_2^{\frac{1}{4}}}\right) \frac{[D_2]}{[HD]} = R_2;$$

for mechanism II (reactions (1) to (6) and (9) to (11))

$$k_{5}/k_{2}^{\frac{1}{2}} = \left(\frac{\text{rate } CF_{3}H}{(\text{rate } C_{2}F_{6})^{\frac{1}{2}}[H_{2}]} - \frac{k_{3}}{k_{2}^{\frac{1}{2}}}\right)\frac{[H_{2}]}{[HD]} = R_{3},$$

$$k_{6}/k_{2}^{\frac{1}{2}} = \left(\frac{\text{rate } CF_{3}D}{(\text{rate } C_{2}F_{6})^{\frac{1}{2}}[D_{2}]} - \frac{k_{4}}{k_{2}^{\frac{1}{2}}}\right)\frac{[D_{2}]}{[HD]} = R_{4}.$$

Since we know k_3 and k_4 from experiments with hydrogen and deuterium alone, we can evaluate each of these functions. It will be seen that, because of the difference in the two methods of calculating k_3 and k_4 , $R_1 = R_3$ and $R_2 = R_4$. Reference to table 3 will show that R_1 and R_2 are not equal, as they should be if mechanism I is correct. We suggest, therefore, that the behaviour of the system is more

time (sec)	CF_3COCF_3 moles/cm ³ \times 10 ⁷	H ₂ n	D_2 noles/cm ³ ×	HD 107	C ₂ F ₆ m	products CF ₃ H oles/sec ×	CF3D 1010	$R_1 = R_3$ $k_5/k_2^{\frac{1}{2}}$ $cm^{\frac{3}{2}} mole$
2700	10.21	5.99	4.38	11.0	11.15	1.55	0.394	0.0760
2350	11.20	4·89	3.75	8.40	14.65	2.92	0.648	0.204
2700	9.91	4.49	3.31	8.28	16.85	5.02	1.27	0.320

3.90

5.05

12.5

15.9

3.98

7.57

1.14

2.15

0.729

0.869

TABLE 3

° K

375 394

407.5

2100

2400

10.98

10.87

2.27

2.76

1.74

2.02

432

447

correctly described by mechanism II, which assumes that the hydrogen atoms, etc., disappear by recombination rather than by reaction with trifluoromethyl radicals. In this case we can calculate the four rate constants for the reaction of trifluoromethyl radicals with the hydrogen isotopes. Fig. 1 shows the Arrhenius



FIG. 1.—Arrhenius plots for the reactions of trifluoromethyl radicals with hydrogen isotopes. For clarity the $CF_3 + D_2$ plot has been transposed 0.5 unit downwards.

plots for the four reactions. The rate constants and activation energies are given in table 4, taking $k_2 = 2.3 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ (ref. (11)). Whittle and Steacie's ² values for the same parameters of reactions between methyl radicals and hydrogen are listed in the same table. The limits of error quoted are based on estimates of the limiting slopes of the Arrhenius plots.

TABLE 4

СН₃		E kcal mole ⁻¹	$k_{CH_3}^{400^{\circ}}$ $cm^3 \times 10^{-6}$ $mole^{-1}$ sec^{-1}	CF3		E kcal mole ⁻¹	$k_{\rm CF_3}^{400^\circ}$ cm^3 $\times 10^{-6}$ $mole^{-1}$ sec^{-1}	$\frac{\log k_{\rm CH_3}}{\log k_{\rm CF_3}}$
$+H_2 \rightarrow CH_4$	(a)	10.0 ± 0.5	1.56	$+H_2 \rightarrow CF_3H$	(a')	9·5 ±0·7	4.49	0.931
+HD→CH₄	(b)	10.0 ± 1.0	0.55	+HD→CF ₃ H	(b')	10·5 ±1·5	1.10	0.929
+HD→CH ₃ D	(c)	$11\cdot3\pm1\cdot0$	0.23	$+HD \rightarrow CF_{3}D$	(c')	10.2 ± 1.5	0.564	0.932
$+D_2 \rightarrow CH_3D$	(d)	11·8±0·5	0.33	$+D_2 \rightarrow CF_3D$	(d')	10.2 ± 0.7	0.762	0.938

The Arrhenius equation in its thermodynamic formulation is

$$k_r = \frac{kT}{h} \exp\left(-\frac{\Delta F^*}{RT}\right),$$

where ΔF^* is the free energy of activation. The ratio (log $k_{CH_3}/\log k_{CF_3}$) given

in the final column of table 4 is therefore equal to $(\Delta F^*_{CF_3}/\Delta F^*_{CH_3})$, i.e. the fractional decrease in free energy of activation on passing from the methyl to the trifluoromethyl reaction in each of the four cases *a*, *b*, *c*, *d*; *a'*, *b'*, *c'*, *d'*. The figures listed show that

$$\Delta F_{CF_3}^* = (0.933 \pm 0.005) \Delta F_{CH_3}^*$$

This constant decrease in free energy of activation constitutes a close parallelism between the methyl reactions a, b, c, d and the fluoromethyl reactions a', b', c', d', and lends weight to the argument that the quantities being measured are the reaction rates for the specified reactions and not the rates of the various possible side reactions.

CALCULATIONS BASED ON THE COLLISION THEORY OF REACTION RATES

Making use of the collision diameters CF_3 , $4\cdot 0$ Å; H_2 , $2\cdot 8$ Å; we have calculated collision numbers for the four reactions a', b', c', d'. The same collision diameter was used for H_2 , D_2 and HD. A factor of a half was introduced into the collision expression for the reactions with HD to indicate that only collisions with one end of the molecule are to be considered. With these assumptions we obtain the pre-exponential factors listed in table 5. The absolute values are several orders of magnitude in error, the observed values being about 5×10^{11} .

TABLE 5					
reaction :	a'	b'	c'	ď	
A (400° K) collision theory, \times 10 ⁻¹⁴	4.57	1.88	1.88	3.28	

This discrepancy is expressed as a steric factor $\sim 10^{-3}$. The relative (calculated) values, taking A (400° K) for CF₃ + H₂ as 1.0, are 1.0:0.4:0.4:0.7. In order for our observed rate constants to be consistent with these relative values for A (400° K) it would be necessary for the activation energy for the reaction CF₃ + D₂ (d') to be 1.2 kcal mole⁻¹ greater than that for CF₃ + H₂ (a'). Our results indicate a difference of 0.7 kcal mole⁻¹ but, in view of the errors in the two determinations, further experiments would be necessary to decide whether this figure is significant.

CALCULATIONS BASED ON THE ABSOLUTE THEORY OF REACTION RATES

Our results may also be compared with the pre-exponential factors calculated on the basis of the absolute theory of reaction rates. In order to do this the various terms in the entropies of activation for the four reactions studied in this work have been calculated. The calculation followed the lines of that made previously on

TABLE 6

INITIAL STATE ENTROPIES (cal/mole deg.)

	s_T°	s_R°	s_E°	$s^{\circ}_{T,R,E}$
H_2	29.5	3.6		33.1
HD	30.8	5.6		36.4
D_2	31.6	5.0		36.6
CF ₃	40 ∙1	21.5	1.4	63·0

the analogous series of reactions between CH_3 and hydrogen and between CD_3 and hydrogen.³ The method of calculation involves the use of a calibrated "symmetrical" potential energy surface in which the percentage coulombic energy

P. B. AYSCOUGH AND J. C. POLANYI

is adjusted so that there is no longer any potential energy basin corresponding to a molecule of the type CF_3H_2 . The characteristics of this model and the restrictions implicit in it are discussed fully in the earlier paper. The initial state and transition state entropies are listed in tables 6 and 7. The subscripts *T*, *R*, *V*, *E*, refer to translational, rotational, vibrational and electronic degrees of freedom respectively.

TABLE 7

TRANSITION STATE ENTROPIES (cal/mole deg.)

s_T^*	s_R^*	s_V^*	s_E^*	^{\$} T, R, V, E	$-\Delta S_p$	A (400° K) × 10 ⁻¹¹
40·2	23.3	0.2	1.4	65.4	30.7	3.75
40.2	23.4	0.6	1.4	65.6	33.8	0.79
40·2	23.3	0.62	1.4	65·5 ₅	33·8 ₅	0.77
40.3	23·4 ₅	0.7	1.4	65·8 ₅	33·7 ₅	0.81
	s [*] _T 40·2 40·2 40·2 40·3	$\begin{array}{ccc} s_{T}^{*} & s_{R}^{*} \\ 40.2 & 23.3 \\ 40.2 & 23.4 \\ 40.2 & 23.3 \\ 40.3 & 23.4_{5} \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Entropies of activation for the various degrees of freedom are plotted in fig. 2, both for CH₃ as the attacking group (reactions *a*, *b*, *c*, *d*; see table 4), and for CF₃ as the attacking group (reactions a', b', c', d').



FIG. 2.-Entropies of activation for reactions of CF3 and CH3 with hydrogen isotopes.

Calculation of the entropy terms involves similar approximations to those made in the work on methyl and hydrogen. Translational entropies are accurately calculable for both initial state and transition state. Calculation of rotational entropies for the initial state were made on the assumption of planar CF_3 , in conformity with the earlier calculation. The observation that CF_3 dimerizes at the same rate as CH_3 ¹¹ cannot be taken as evidence that the radicals

are non-polar and for this reason not subject to steric hindrance due to replacement of H by F. All that can be said is that the transition state complex is sufficiently extended along the reaction co-ordinate for the F atoms on opposing CF₃ groups not to obstruct one another. The case is similar to the observation of Garvin and Kistiakowsky ¹³ that BF₃ and dimethylamine combine at a rate comparable to the rate of dimerization of methyl radicals, indicating a large separation along the reaction co-ordinate in the transition state complex.

A three-dimensional model of the transition-state complex was used in the calculation of the rotational entropy. The angle between the CF3 "umbrella" and the C-H-H axis was taken as 109.5°. The C-H and H-H separations in the transition state were taken respectively as 1.25 Å and 0.84 Å (this corresponds to the "symmetrically stretched" configuration of CH₃-H-H). The C-F separation in the initial state and transition state was taken as 1.40 Å (Herzberg ¹⁴ gives a value $r_0(C-F) = 1.39_8$ Å for the equilibrium separation of C-F in CH_3F obtained on the assumption that the C-H distance in CH_3F is the same as in CH₄. Bailey, Hale and Thompson ¹⁵ cite values for the C--F separation in CH₃F, $r_0(C-F) = 1.42$ Å and in CF₄, $r_0(C-F) = 1.36$ Å, both taken from electron diffraction data.) In calculating the vibrational entropy of activation it has been assumed, as in the earlier calculation, that the modifications undergone by the characteristic frequencies of the CF_3 in entering the transitionstate complex are small and are not significantly different in the various reactions, i.e. the CF_3 vibrations can be considered separately from those in the remainder Probably this is the weakest point in the calculation. Stretching of the molecule. frequencies in the remainder of the molecule have negligible entropy, but the two degenerate frequencies of bending about the central atom make an appreciable contribution to the total entropy of activation. The bending force constant was taken to be the same for CF_3 —H—H as for CH_3 —H—H (8·1 kcal mole⁻¹ rad⁻²) and the calculation followed that used for the latter complex.

TABLE 8

PRE-EXPONENTIAL FACTORS A (400° K) for hydrogen-abstraction reactions

	calc.	obs.
$H + H_2$	6.0×10^{13} *	$5.4 imes10^{13}$ ‡
$CH_3 + H_2$	1·9 × 10 ¹² *	$1.6 imes10^{12}$ *
$\mathrm{CF}_3 + \mathrm{H}_2$	$3.8 imes10^{11}$ †	> 3·0 $ imes$ 10 ¹¹ †

* ref. (3); see also Bywater and Roberts.¹⁶

† this work; if we take E = 9.5, $A_{obs}^{400^{\circ} \text{K}} = 7.2 \times 10^{11}$.

‡ ref. (17). This value is taken from $k(1000^{\circ} \text{ K})$; however, variation in A even over this temperature range will fall outside the limits of accuracy for activation-energy determination (viz., ± 0.4 kcal) and hence can be ignored.

The absolute value of the pre-exponential factor $A (400^{\circ} \text{ K})$ obtained by this method is lower by 10^{-3} than that obtained from the collision theory. In table 8 pre-exponential factors calculated by the "absolute method" are listed alongside the experimental data for the three reactions : $H + H_2$, $CH_3 + H_2$, and $CF_3 + H_2$. The progressive decrease in A predicted by the theory is confirmed by the experimental values, though for CF_3 the agreement is best if we take the lowest activation energy consistent with experiment. We choose this value for E on the grounds that in all the previous cases for which hydrogen abstraction by CF_3 has been investigated ⁴⁻⁷ the activation energy has been found to be 2-3 kcal mole⁻¹ less than for the analogous reaction of CH_3 . On the basis of the activation energies for the reactions of methyl with hydrogen we would expect E = 8-9 kcal mole⁻¹ for the present reaction. Using the lowest activation energy consistent with our experiments we have for CF₃ + H₂, E = 8.8 kcal mole⁻¹ * and A (400° K) = 3.0×10^{11} cm³ mole⁻¹ sec⁻¹.

Independent evidence for a sequence of decreasing pre-exponential factors similar to that shown in table 8 comes from work of Sieger and Calvert.⁷ These workers photolyzed trifluoroacetone and were able to observe the reactions

$$CH_3 + CH_3COCF_3 \rightarrow CH_4 + CH_2COCF_3$$
 (1)

$$CF_3 + CH_3COCF_3 \rightarrow CF_3H + CH_2COCF_3$$
 (2)

in the same system. If the steric factors for CH₃ dimerization and CF₃ dimerization are the same, then they obtain the ratio of steric factors $P_1/P_2 = 5/1$. Since the collision numbers will be in the ratio $\mu_2^{\frac{1}{2}}/\mu_1^{\frac{1}{2}} = 1.8/1$ (μ is the reduced mass) it follows that the pre-exponential factors are in the ratio $A_1/A_2 = 9/1$. (Sieger and Calvert took $\sigma_{CH_3} = \sigma_{CF_3}$.) This may be compared with the predicted ratio of pre-exponential factors (5/1, see table 8) for the reactions CH₃ + H₂ and CF₃ + H₂.

In order to compare the calculated pre-exponential factors for the four reactions a', b', c', d', with the experimental values it is necessary to make some assumption about the activation energies since these are not known with sufficient accuracy. In the analogous reactions of CH₃ and CD₃ it was found that there was fair agreement between theory and experiment assuming constant activation energy, but that the correlation was improved by permitting a rise of about 0.7 kcal mole⁻¹ along the isotopic series. This was in general accord with the observed activation energies though again these were not accurate enough to provide a good test. We again choose constant activation energy as the basis for the first test of our calculations, to be amended later if the correlation can be improved. It should be emphasized that the theoretical treatment makes no predictions concerning the activation energies except that the differences are small. It would therefore be more correct to discuss the correlation between A_{calc} and k_{obs} .

The relative values for the pre-exponential factors obtained on the absolute theory (table 7), taking A for $CF_3 + H_2$ as unity, are $1.0: 0.21: 0.20_5: 0.21_5$. Relative pre-exponential factors taken from the experimental rate constants in conjunction with constant activation energy are 1.0:0.24:0.13:0.17. These experimental ratios of A's are the same whatever (constant) value of E is taken in the range 10.1 ± 1.0 kcal mole⁻¹. The first reaction in the series is correctly given by the theory as having a substantially higher A value than the second member of the series; the ratio of A's according to theory is 4.75/1, from experiment 4.0/1 (on the collision theory the ratio was 2.5/1). The A values for the last three members of the series (reactions b', c', d' of table 4) are almost constant according to theory, whereas the experimental values, based on constant activation energy, vary by almost 100 %. As far as the theoretical values are concerned this constancy can be seen from fig. 2 to be due to the fact that the vibrational entropy of activation is apparently fairly constant along the series b', c' d', while the upward trend in rotational entropy of activation almost exactly counteracts the downward trend in translational entropy of activation. The discrepancy between the relative values of the calculated A's, and the relative values of the " observed " A's obtained on the assumption of constant activation energy would be eliminated if reactions c' and d' had activation energies 0.4 and 0.2 kcal mole⁻¹

^{*} We learn that Pritchard, Pritchard, Schiff and Trotman-Dickenson, in a study of the photolysis of perfluoroazomethane in the presence of hydrogen and deuterium, find for $CF_3 + H_2$, E = 8.8 kcal mole⁻¹ and for $CF_3 + D_2$, E = 9.7 kcal mole⁻¹ in good agreement with our lowest values. We are grateful to these authors for permission to quote their results before publication.

respectively, greater than a'. Such a difference certainly cannot be excluded on the basis of our experiments. It is not possible to say whether the discrepancy between the A values calculated and observed arises from a shortcoming in the theoretical treatment or in the experimental method.

It is interesting to note how very insensitive the transition state entropy is in these reactions to replacement of H by D. In the reactions $H + H_2$, etc., and the reactions $CH_3 + H_2$, etc., the variation in total transition state entropy down the isotopic series is ± 1 cal/mole deg. In the present series it is ± 0.2 cal/mole The changes in the total entropy of activation are almost entirely determined deg. by changes in the entropy of the initial state. The calculation suggests that this result will be general for heavier radicals reacting with hydrogen isotopes. For these reactions it should be possible to account for changes in pre-exponential factor simply in terms of changing entropy of the reactants H₂, HD, D₂. On this basis the expected relative pre-exponential factors are: $R + H_2 \rightarrow RH$, A = 1.0; R + HD \rightarrow RH, A = 0.19; R + HD \rightarrow RD, A = 0.19; R + D₂ \rightarrow RD, A = 0.17. These figures differ only slightly from those obtained from the detailed calculation given above.

We wish to thank Dr. E. W. R. Steacie for helpful discussions and much encouragement in this work We are also indebted to Boato, Caveri, Cimino, Molinari and Volpi for permission to quote their results before publication.

- ¹ Majury and Steacie, Faraday Soc., 1953, 14, 45.
- ² Whittle and Steacie, J. Chem. Physics, 1953, 21, 993.
- ³ Polanyi, J. C., J. Chem. Physics, 1955, 23, 1505; J. Chem. Physics, 1956, 24, 493.
- ⁴ Ayscough, Polanyi, J. C. and Steacie, Can. J. Chem., 1955, 33, 743.
- ⁵ Ayscough and Steacie, Can. J. Chem., 1956, 34, 103.
- ⁶ Pritchard, Pritchard and Trotman-Dickenson, Chem. and Ind., 1955, 564.
- ⁷ Sieger and Calvert, J. Amer. Chem. Soc., 1954, 76, 5197.
- ⁸ Morse, Ayscough and Leitch, Can. J. Chem., 1955, 33, 453.
- 9 Ayscough, Can. J. Chem., 1955, 33, 1566.
- ¹⁰ Ayscough and Steacie, Proc. Roy. Soc. A, 1956, 234, 476.
- ¹¹ Ayscough, J. Chem. Physics, 1956, 24, 944.
- 12 Majury and Steacie, Can. J. Chem., 1952, 30, 800.
- 13 Garvin and Kistiakowsky, J. Chem. Physics, 1952, 20, 105.
- ¹⁴ Herzberg, Infra-red and Raman Spectra (D. Van Norstrand Co., New York, 1945).
- ¹⁵ Bailey, Hale and Thompson, Proc. Roy. Soc. A, 1938, 167, 555.
- ¹⁶ Bywater and Roberts, Can. J. Chem., 1952, 30, 773.
- 17 Boato, Caveri, Cimino, Molinari and Volpi, J. Chem. Physics, in press.