Reactions of Trifluoromethyl Radicals with Organic Halides

Part 5.—Fluoromethanes and Fluoroethanes

BY R. D. GILES,* L. M. QUICK AND E. WHITTLE

Chemistry Dept., University College, Cathays Park, Cardiff

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Hexafluoroacetone has been photolyzed in the presence of CH₄, CH₃F, CH₂F₂, CF₃CH₃, CF₂HCF₂H and CF₃CF₂H. Arrhenius parameters are obtained for the abstraction of H by CF₃ radicals using the combination of CF₃ radicals as a reference reaction. Results were checked by photolysis of hexafluoroacetone in the presence of CD₄ plus each of the fluoroethanes and CH₄ in turn and using the reaction, CF₃+CD₄→CF₃D+CD₃, as a reference. The activation energies obtained are compared with those for related series involving abstraction of H by CF₃ and CH₃ radicals and by bromine atoms.

The secondary products of the system $CF_3 + CH_2F_2$ have been measured. For the combination and cross-combination reactions of CF_3 and CHF_2 radicals, we obtain $\phi = 2.4$ independent of temperature in the range 291-363°C. It is concluded that the second of the reactions

$$CF_3+CHF_2$$

 $CF_2=CF_2+HF$

occurs to a negligible extent.

Previous papers have dealt with the reactions of CF_3 radicals with halogenated methanes ¹⁻³ and aromatic halides.⁴ None of these compounds contained fluorine so we have now studied the reactions of CF_3 radicals with fluoromethanes and fluoroethanes; the results are given in this paper.

EXPERIMENTAL

MATERIALS

Most of these were prepared and purified as described elsewhere.⁵⁻⁷ A sample of CF₂== CHF was kindly donated by Prof. Haszeldine of the University of Manchester. C_3F_8 and $n-C_4F_{10}$ were from Peninsular ChemResearch, Florida, U.S.A. CD₄ was made from D_2O+CCl_4+Zn dust by the method of Leblanc *et al.*⁸ It was passed through a trap at $-80^{\circ}C$ into a trap cooled in solid nitrogen. The CD₄ was purified by several distillations from -183 to $-210^{\circ}C$. Two samples were made which were analyzed by mass spectrometer to contain 96 % CD₄, 4 % CD₃H and 95 % CD₄, 5 % CD₃H respectively. Each reactant (except hexafluoroacetone) was freed of possible traces of acids by passing the gas through Carbosorb. All were better than 99 % pure as indicated by i.-r. and g.s.c.

APPARATUS AND PROCEDURE

These were as described elsewhere.⁹ The reaction products were fractionated by means of two Ward stills in series and each fraction was analyzed quantitatively by g.s.c. using an alumina column; further details appear later in the paper.

* present address : Midland Silicones, Barry, Glam.

R. D. GILES, L. M. QUICK AND E. WHITTLE

RESULTS AND DISCUSSION

When hexafluoroacetone HFA is photolyzed in presence of a compound RH, the main reactions are

$$CF_3COCF_3 + hv \rightarrow 2CF_3 + CO \tag{1}$$

$$CF_3 + CF_3 \rightarrow C_2F_6$$
 (2)

$$CF_3 + RH \rightarrow CF_3H + R$$
 (3)

If RH contains a halogen X then CF_3X may be formed by an abstraction reaction analogous to (3). However, in the present work, CF4 was never detected in the products, hence abstraction of fluorine is negligible under our conditions.

If C_2F_6 and CF_3H are formed only by reactions (2) and (3) respectively, then

$$k_{\rm H}/k_c^{\frac{1}{2}} = R_{\rm CF_{3}H}/R_{\rm C_{2}F_{6}}^{\frac{1}{2}}[\rm RH], \tag{4}$$

where $k_{\rm H}$ and k_c are rate constants for H abstraction and combination of CF₃ radicals respectively. The compounds studied were CH4, CH3F, CH2F2, CD4, CF3CH3, CF_2HCF_2H and CF_3CF_2H ; in each, the point at which H abstraction occurs is unambiguous. The products always included CO, C_2F_6 and CF_3H and the ratio $k_{\rm H}/k_c^{1}$ was measured over a range of temperatures. The Arrhenius plots were good straight lines which yielded the results in table 1.

TABLE 1.—Arrhenius parameters for abstraction of H by CF_3 from fluoroalkanes

RH	temp. range, °C	no. of runs	$E_{\rm H} - \frac{1}{2}E_c$	$A_{\rm H}/A_{c}^{\frac{1}{2}} \times 10^{-5}$
*CH4	—		11.3 ± 0.5	1·9 ±0·9
CH ₃ F	196-359	10	11.2 ± 0.2	2.8 ± 0.6
CH_2F_2	175-363	10	11.2 ± 0.3	1.5 ± 0.4
CF ₃ CH ₃	293-405	17	15.8 ± 0.2	18 ± 5
CF ₂ HCF ₂ H	237-410	6	12.4 ± 0.3	1·9 ±0·4
CF ₃ CF ₂ H	234-451	7	11.5 ± 0.3	0·40 ±0·10

 $E_{\rm H} - \frac{1}{2}E_c$ in kcal mole⁻¹; $A_{\rm H}/A_c^{\frac{1}{2}}$ in cm^{$\frac{3}{2}$} mole^{- $\frac{1}{2}$} sec^{- $\frac{1}{2}$}. * from ref. (1).

Attempts were made to identify final products derived from the radical R which is formed by reaction (3). However, analyses were difficult because the fluoroalkanes used as reactants have volatilities similar to those of the products. The amount of reactant decomposed was always ≤ 3 % so g.s.c. analyses were necessarily done with a mixture containing at least 97 % of unchanged reactant. Details of products identified are as follows.

 $CF_3 + CF_2H_2$

Abstraction of H was studied in the range 175-363°C. Above 290°, the products included CF_3CF_2H and CF_2HCF_2H which were identified by i.-r. and g.s.c.; the latter was also used for quantitative analyses. Using an alumina column with H_2 as carrier gas, the order of elution was; 1, $(CF_3H+C_2F_6+unreacted CF_2H_2)$; 2, CF_3CF_2H ; 3, CF_2HCF_2H . Another more active alumina column was used to analyze the $CF_3H + C_2F_6 + CF_2H_2$,

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At higher temperatures, R_{CF_3H} was found to exceed $R_{C_2F_6}$ so that CF₃ radicals disappear largely by the reaction,

$$CF_3 + CF_2H_2 \rightarrow CF_3H + CF_2H.$$
(5)

Thus, the stationary concentration of CF_2H radicals is appreciable and the following reactions

$$CF_3 + CF_2H \rightarrow CF_3CF_2H$$
 (6)

$$CF_2H + CF_2H \rightarrow CF_2HCF_2H$$
 (7)

should occur. We define the ϕ factor for the combination and cross-combination of CF₃ and CF₂H in the usual way:

$$\phi = k_6 / (k_c k_7)^{\frac{1}{2}} = R_{\text{CF}_3 \text{CF}_2 \text{H}} / (R_{\text{C}_2 \text{F}_6} R_{\text{CF}_2 \text{H} \text{CF}_2 \text{H}})^{\frac{1}{2}}.$$
(8)

Values of ϕ were obtained over the range 291-363°C and the average was 2.4. Within experimental error, ϕ was independent of temperature. From collision theory, $\phi = 1.9$, if we use collision diameters of 4.0 Å for both CF₃ and CF₂H. This agrees with the experimental result and suggests that $E_c = E_6 = E_7 = 0$.

Fluorinated methyl radicals undergo elimination reactions as well as the usual combination reactions,^{10, 11} e.g.,

$$CH_2F + CH_2F \rightarrow CH_2 = CHF + HF$$
(9)

$$CF_3 + CH_3 \rightarrow CF_2 = CH_2 + HF.$$
(10)

The analogues of these involving CF₂H are

 $CF_2H + CF_2H \rightarrow CF_2 = CHF + HF$ (11)

$$CF_3 + CF_2 H \rightarrow CF_2 = CF_2 + HF.$$
 (12)

The occurrence of reactions (11) and (12) would invalidate ¹¹ our calculation of ϕ by means of eqn. (8). However, neither CF₂==CHF nor CF₂==CF₂ was detected in our products. Tests with authentic samples of these olefines showed that they would have been detected by g.s.c. if present in amounts exceeding 0.7 % of the corresponding CF₂HCF₂H and CF₃CF₂H. We therefore conclude that the elimination reactions (11) and (12) occur much less rapidly than the corresponding elimination reactions (9) and (10). This agrees with the findings of Bryant and Pritchard ¹² who studied the photolysis of (CF₂H)₂CO and showed that the products contained CF₂HCF₂H but not CF₂==CHF. Reactions (9)-(12) were considered theoretically by Benson and Haugen ¹³ who likewise concluded that the elimination reaction (11) should be of little importance compared with reaction (7). Our work also indicates that the elimination reaction (12) is unimportant compared with reaction (6).

When HFA is photolyzed, it follows from eqn. (1) that $R_{CF_3} = 2R_{CO}$. In the system HFA + CF₂H₂, the measured products containing CF₃ were C₂F₆, CF₃H and CF₃CF₂H and we can calculate a CF₃ balance given by

$$CF_3$$
 balance = $(2R_{C_2F_6} + R_{CF_3H} + R_{CF_3CF_2H})/R_{CO}$.

This ratio should be ≤ 2 depending on whether all the CF₃ radicals originally produced have been accounted for in the final products. The CF₃ balance calculated using the above eqn. was 1.9 at 291°C and rose progressively to 2.9 at 363°C. As the temperature rises, $k_{\rm H}$ increases, hence reaction (3) is faster and this in turn should decrease the stationary concentration of CF₃ radicals and therefore $R_{\rm C_2F_6}$; in fact, $R_{\rm C_2F_6}$ was virtually constant in the range 291-363°C. These facts imply the existence of a chain

reaction which produces CF_3 but not CO and we suggest that this could involve the reaction,

$$CF_{2}H$$

$$\downarrow CF_{3}COCF_{3} \rightarrow CF_{3} \rightarrow CF_{3} \rightarrow CF_{3}COCF_{2}H + CF_{3} \qquad (13)$$

$$\downarrow O$$

which re-generates the CF_3 radicals consumed by reaction (5). The analogous reaction

 $CH_3 + CF_3COCF_3 \rightarrow CH_3COCF_3 + CF_3$

was observed by Alcock and Whittle.1

 $CF_3 + CH_3F$

In addition to CO, C_2F_6 and CF_3H , three unknowns were detected by g.s.c. in amounts which increased at higher temperatures. They were probably CF_3CH_2F and CH_2FCH_2F or adducts of radicals to olefines formed by reactions such as (9). Authentic samples of these compounds were not available. At the highest temperatures used (>350°C) the CF₃ balance again exceeded 2 even though other products containing CF₃ were probably present but were not measured. This again suggests a chain sequence involving the analogue of reaction (13) in which CH₂F displaces CF₃.

$CF_3 + C_2F_5H$ or CF_2HCF_2H

With HFA+C₂F₅H, the products at higher temperatures included C₃F₈ which was identified by i.-r. and g.s.c. At the highest temperature of 451°C, the other expected radical combination product $n-C_4F_{10}$ was detected but in amounts too small to measure. No secondary products were identified in the system HFA+CF₂HCF₂H.

$CF_3 + CF_3CH_3$

Preliminary experiments indicated that $E_{\rm H} - \frac{1}{2}E_c \sim 17$ kcal mole⁻¹ and $A_{\rm H}/A_c^{1} \sim 5 \times 10^6$ cm³ mole⁻¹ sec⁻¹ both of which are much larger than the values for the other compounds (see table 1). In view of this, the kinetics were studied in detail to see if eqn. (4) is valid in this system. At the lower end of the temperature range, 5 runs were done in which the HFA and CF₃CH₃ pressures were varied in the ranges 21-42 mm and 20-105 mm respectively at 296°C; similarly in 6 runs at 400°C, the pressure ranges covered were 20-50 mm (HFA) and 20-94 mm (CF₃CH₃). Values of $k_{\rm H}/k_c^{1}$ varied randomly by ± 8 % at 296° and ± 12 % at 400°C, hence there were no significant changes in $k_{\rm H}/k_c^{1}$ when the concentrations of reactants or total pressure were changed. Results from these and other runs lead to Arrhenius parameters given in table 1; the preliminary high values of $E_{\rm H} - \frac{1}{2}E_c$ and $A_{\rm H}/A_c^{1}$ given above thus appear to be confirmed.

Complications which could invalidate the use of eqn. (4) are as follows. From a study of the pyrolysis of CF₃CHO, Arthur and Bell ¹⁴ proposed that above 470°C the combination of CF₃ radicals, reaction (2), requires a third body at pressures similar to those used by us. This would invalidate the use of eqn. (4) if it were also true in our temperature range; however, our results indicate no dependence on pressure hence we conclude that a third body is not needed below 400°C.

If the value of $E_{\rm H} - \frac{1}{2}E_c$ in table 1 were indeed larger than the true figure, this would suggest that the values of $k_{\rm H}/k_c^{\frac{1}{2}}$ obtained at higher temperatures are too large. This would happen if "extra " CF₃H were formed by a reaction other than abstraction of

H from CF_3CH_3 by CF_3 , for example, by a disproportionation reaction. The obvious disproportionations are

$$\mathcal{C}F_3 + \mathcal{C}F_3 CH$$
 (14)
CF₃+CF₃CH₂

$$CF_4 + CF_2 = CH_2$$
 (15)

Reaction (14) is unlikely since it gives an ethylidene radical instead of an olefine. Reaction (15) would not interfere but does not actually occur since no CF_4 was formed. Another possible source of extra CF_3H is the sequence,

$$CF_3CH_3 \rightarrow CF_2 = CH_2 + HF$$
 (16)

$$CF_3 + HF \rightarrow CF_3H + F. \tag{17}$$

To test this, a sample of CF₃CH₃ was left in the reaction vessel for 24 h at 400°C (the photolysis time normally used was $\sim \frac{1}{2}$ h). The i.-r. spectrum of the CF₃CH₃ was unchanged after this treatment. Other tests showed that the stock CF₃CH₃ contained no C₂F₆ or CF₃H.

Even if HF were produced by a reaction other than (16), reaction (17) would not make a significant contribution to the CF₃H production since it is endothermic by at least 20 kcal mole⁻¹, hence $E_{17} \ge 20$ kcal mole⁻¹ and the reaction would be far slower than the abstraction of H from CF₃CH₃.

PHOTOLYSIS OF HFA with fluoroalkanes $+ CD_4$

From table 1, within experimental error, the A factors for abstraction of H by CF₃ from CH₄, CH₃F and CH₂F₂ are consistent with the fact that the numbers of available hydrogen atoms are in the ratio 4:3:2. On the other hand, for the fluoroethanes, $A_{\rm H}$ apparently varies by a factor of ~45. An independent check on the results for fluoroethanes seemed desirable and we have therefore photolysed HFA in the presence of CD₄ plus each fluoroethane and also in the presence of mixtures of CD₄+CH₄. For the system HFA+CD₄+RH, the reactions of interest are

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

$$CF_3 + RH \rightarrow CF_3H + R$$
 (3)

$$CF_3 + CD_4 \rightarrow CF_3D + CD_3,$$
 (18)

so that in addition to eqn. (4) we have

$$k_{\rm D}/k_c^{\pm} = R_{\rm CF_3D}/R_{\rm C_2F_6}^{\pm}[\rm CD_4],$$
 (19)

$$k_{\rm H}/k_{\rm D} = R_{\rm CF_3H}[\rm CD_4]/R_{\rm CF_3D}[\rm RH], \qquad (20)$$

where k_c refers to reaction (2) and k_D refers to deuterium abstraction, reaction (18).

When HFA was photolyzed with CD_4 only, the fluoroform produced contained CF_3D and also CF_3H because of the CD_3H impurity in the CD_4 . The ratio $[CF_3H]/[CF_3D]$ was measured using an A.E.I. MS3 mass spectrometer. In 3 runs using ~33 mm HFA and ~26 mm CD_4 , the ratio at various temperatures was, 0.104 at 184°, 0.093 at 284° and 0.124 at 362°C. In all runs with CD_4 + fluoroalkanes, these results were used to correct the measured CF_3H for the small amount of CF_3H produced from CD_3H ; this correction was minimized by making the initial ratio $[RH]/[CD_4]$ as large as possible.

HFA was photolyzed with CD_4 +various RH in turn, with approximate experimental conditions as follows: RH=CH₄, ratio [CH₄]₀/[CD₄]₀ = 2-4, temp. range

139-360°C, 7 runs; RH=CF₃CH₃, [CF₃CH₃]₀/[CD₄]₀ = 2-5, range 150-400°C, 8 runs; RH=CF₂HCF₂H, ratio [CF₂HCF₂H]₀/[CD₄]₀ = 2-5.5, range 144-382°C, 9 runs; RH=CF₃CF₂H, [CF₃CF₂H]₀/[CD₄]₀ = 1.5-2.3, 6 runs. After a run, the products were condensed in liquid nitrogen and the CO+CD₄ were pumped away (also the CH₄ if present). A fraction was subsequently removed with the Ward stills at -145 and -150°C respectively. In the CD₄+CH₄ experiments this fraction contained only C₂F₆+fluoroform. With CD₄+CF₂HCF₂H or CF₃CH₃, traces of the fluoroethanes were also present but not in quantities sufficient to interfere with the analysis. In all these experiments, the -150°C fraction was measured in a gas burette and then divided quantitatively into two parts. One part was analyzed by g.s.c. to give total yields of C₂F₆ and fluoroform and the other was analyzed by mass spectrometer to give the ratio [CF₃H]/[CF₃D]. Thus the absolute yields of C₂F₆, CF₃H and CF₃D were measured so that the rate constant ratios $k_{\rm H}/k_c^{2}$, $k_{\rm D}/k_c^{4}$ and $k_{\rm H}/k_{\rm D}$ were determined for each system.



FIG. 1.—Arrhenius plots of $k_{\rm H}/k_{\rm D}$ for mixtures of CD₄+RH. Curve A, X = 0, RH=CF₃CH₃; curve B, X = 0, RH=CF₂HCF₂H; curve C, X = 0.2, RH=C₂F₅H; curve D, X = 0, RH=CH₄

The procedure was modified for the system $HFA + CD_4 + CF_3CF_2H$ for which the ratio $[CF_3H]/[CF_3D]$ was measured but the yield of C_2F_6 was not, because of the following analytical difficulty. When a mixture of fluoroform and C_2F_6 is distilled from a Ward still at -150° C, the fluoroform is removed readily whereas C_2F_6 requires prolonged pumping. However, at -150° C, CF_3CF_2H is sufficiently volatile to be removed by this pumping (unlike the other two fluoroethanes used) and its presence in the fraction interferes with the CF_3H/CF_3D analysis. Consequently the Ward stills were set at -150 and -160° C and quantitative removal of C_2F_6 was not attempted. The fluoroform removed contained a little CF_3CF_2H which contributed to mass peak 51. This was corrected for using the height of the 104 peak together with the separately measured ratio of the heights of the peaks 51 and 104 for CF_3CF_2H .

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For each series of experiments, the Arrhenius plots of $k_{\rm H}/k_{\rm D}$ are given in fig. 1. Arrhenius plots of $k_{\rm H}/k_c^{\pm}$ for the fluoroethanes are shown in fig. 2 which includes results obtained in the presence of CD4 and also in its absence (from the first part of the paper). Values of $E_D - \frac{1}{2}E_c$ and $A_D/A_c^{\frac{1}{2}}$ obtained in the presence of each RH in turn are given in table 2.





FIG. 2.—Arrhenius plots of $k_{\rm H}/k_c^{1/2}$ for fluoroethanes. Curve A, X = 2, RH=C₂F₅H; curve B, $X = 2\cdot5$, RH=CF₂HCF₂H; curve C, $X = 3\cdot7$, RH=CF₃CH₃. \bigcirc , CD₄ absent; \bigcirc , CD₄ present. On curve C, the points numbered 5 and 6 are the averages of results of 5 and 6 runs respectively. The three lines shown are from least-squares treatment of results obtained with CD₄ absent. $k_{\rm H}/k_c^{\frac{1}{2}}$ in cm³ mole⁻¹ sec⁻¹.

TABLE 2.—ARRHENIUS PARAMETERS FOR REACTION OF CF_3 radicals with CD_4 and FLUOROALKANES

		CF ₃ +RH CF ₃ +CD ₄ CF ₃ +CF ₃ -	$\rightarrow CF_3H + R$ $\rightarrow CF_3D + CD_3$ $\rightarrow C_2F_6$	$k_{\rm H} \\ k_{\rm D} \\ k_c$		
RH	$E_{\rm D} - E_{\rm H}$	$E_{\mathbf{D}} - \frac{1}{2}E_{\mathbf{c}}$	$E_{\mathbf{H}} - \frac{1}{2}E_{\mathbf{c}}$	$A_{\rm H}/A_{\rm D}$	$A_{\mathbf{D}}/A_{c}^{\frac{1}{2}}$	$A_{\rm H}/A_c^{1\over 2}$
					×1	0-5
CH4	1.7 ± 0.1	13.2 ± 0.3	11·5 ±0·3	1.34 ± 0.13	$2 \cdot 4 \pm 1 \cdot 0$	$3 \cdot 2 \pm 1 \cdot 0$
CF ₃ CH ₃	$-(0.2\pm0.2)$	14·3 ±0·3	14·5 ±0·3	1·11 ±0·12	$6 \cdot 2 \pm 2 \cdot 0$	6·9 ±2·0
CF ₂ HCF ₂ H	1.4±0.3	13.3 ± 0.5	11·9 ±0·3	0.46 ± 0.06	2.7 ± 1.0	1.3 ± 0.5
CF ₃ CF ₂ H	$3 \cdot 2 \pm 0 \cdot 2$			0.103 ± 0.020		

Results in this table are from experiments with mixtures of CD_4 +fluoroalkanes whereas results in table 1 are from experiments with CD4 absent.

Activation energies in kcal mole⁻¹; $A_{\rm H}/A_c^{\frac{1}{2}}$ in cm² mole⁻¹ sec⁻¹.

We now consider the internal consistency of the various results which have been obtained using, (i) eqn. (4), or (ii) a combination of eqn. (19) and (20). Data on reaction (18) which involves CF₃ and CD₄ have been obtained in the presence of CH₄, CF₃CH₃ and CF₂HCF₂H. From table 2, values of $E_D - \frac{1}{2}E_c$ and $A_D/A_c^{\frac{1}{2}}$ obtained when either CH₄ or CF₂HCF₂H is present agree well but agreement is less good if CF₃CH₃ is present. This is illustrated in fig. 3 which shows Arrhenius plots for



FIG. 3.—Arrhenius plots of $k_D/k_{\frac{1}{2}}$ in the presence of various RH. Curve A, X = 2, \bigcirc , RH=CH₄, \odot ; RH=CF₂HCF₂H; +, RH absent. Curve B, X = 2.5, RH=CF₃CH₃. $k_D/k_{\frac{1}{2}}$ in cm² mole⁻¹ sec⁻¹

 k_D/k_c^{\pm} obtained in the presence of CF₃CH₃ and for combined values of k_D/k_c^{\pm} obtained from the systems HFA+CD₄+CH₄, HFA+CD₄+CF₂HCF₂H and HFA+CD₄ only. A least-squares treatment of these combined results (i.e., excluding those with CF₃CH₃ present) gives

 $k_{\rm CD_4}/k_c^{\frac{1}{2}} = (2.7 \pm 1.0) \times 10^5 \exp{-(13,300 \pm 200)/RT} \text{ cm}^{\frac{3}{2}} \text{ mole}^{-\frac{1}{2}} \sec^{-\frac{1}{2}},$ (21) where

 $k_{\rm CD_4} = k_{18}.$

The corresponding reaction involving CH₄ has now been studied by four groups of workers with the following results: $E_{\rm H} - \frac{1}{2}E_c = 10\cdot3,^{15}$ 11·0,¹⁶ 11·3,¹ 11·5 (p.w.) kcal mole⁻¹; $A_{\rm H}/A_c^{\rm 1} = 1\cdot0 \times 10^5, 2\cdot5 \times 10^5, 1\cdot9 \times 10^5, 3\cdot2 \times 10^5$ (p.w.), (p.w. = present work). We therefore recommend the following weighted expression,

$$k_{\rm CH_2}/k_c^{1} = (2.5 \pm 0.8) \times 10^5 \exp(-(11,200 \pm 200)/RT \, {\rm cm}^{3} \, {\rm mole}^{-\frac{1}{2}} \, {\rm sec}^{-\frac{1}{2}}.$$
 (22)

Combining eqn. (21) and (22) gives

$$k_{\rm CH_4}/k_{\rm CD_4} = (0.9 \pm 0.3) \exp(2,100 \pm 300)/RT$$

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whereas we obtain directly (see table 2),

$k_{\rm CH_4}/k_{\rm CD_4} = (1.3 \pm 0.1) \exp(1,700 \pm 100)/RT;$ (23)

the agreement between the two expressions supports the results in eqn. (21) and (22). Carmichael and Johnston ¹⁶ photolyzed HFA with CH₄ and CD₄ separately and obtained $E_{CD_4} - E_{CH_4} = 12 \cdot 1 - 11 \cdot 0 = 1 \cdot 1$ kcal mole⁻¹ and $A_{CH_4}/A_{CD_4} = 6 \cdot 3$. The ratio of A factors seems improbably large and our result in eqn. (23) seems more reasonable particularly as it was obtained using mixtures of CH₄ and CD₄ rather than reacting CF₃ with CH₄ and CD₄ separately. If eqn. (23) is indeed correct it implies an isotope effect in which $E_{CD_4} - E_{CH_4}$ is appreciably greater than the difference between the zero-point energies of the C—D and C—H bonds. This is supported by Sharp and Johnston ¹⁷ who obtained $E_D - E_H = 12 \cdot 7 - 10 \cdot 5 = 2 \cdot 2$ kcal mole⁻¹ for the attack of CF₃ on CD₃H. Furthermore they obtained $A_H/A_D = 0 \cdot 51$ (on a per atom basis).

Eqn. (21) can be combined with eqn. (20) and results for mixtures of HFA+CD₄+ RH to give "calculated" values of $E_{\rm H} - \frac{1}{2}E_c$ and $A_{\rm H}/A_c^{\frac{1}{2}}$ for the fluoroethanes shown in columns 4 and 7 of table 3 which includes for comparison data obtained in the absence of CD₄. Reference to columns 5 and 7 reveals that values of $A_{\rm H}/A_c^{\frac{1}{2}}$ for CF₂HCF₂H and CF₃CF₂H obtained directly, i.e., with CD₄ absent, agree well with those based on CF₃+CD₄ as a reference reaction; this is also true for CH₄ (see tables 1 and 2). However, with CF₃CH₃, the two methods give different results and the value of $A_{\rm H}/A_c^{\frac{1}{2}}$ in the last column of table 3 appears much the more reasonable. Similarly, the value of $E_{\rm H} - \frac{1}{2}E_c$ for CF₃CH₃ obtained using CF₃+CD₄ as a reference seems more reliable.

TABLE 3.—COMPARISON OF ARRHENIUS PARAMETERS FOR ABSTRACTION OF H FROM FLUOROETHANES

RH	$E_{H} - \frac{1}{2}E_{c}$ (obs.) CD ₄ absent	$E_{\mathbf{D}} - E_{\mathbf{H}}$ obs.	$E_{\mathbf{H}} - \frac{1}{2}E_{c}$ calc.	$A_{\rm H}/A_c^{\frac{1}{2}}$ (obs.) CD ₄ absent $\times 10^{-5}$	AH/AD obs.	$A_{\rm H}/A_c^{1\over c}$ (calc.) ×10 ⁻⁵
CF ₃ CH ₃	15.8	-0.2	13.5	18	1.11	3.0
CF ₂ HCF ₂ H	12.4	1.4	11.9	1.9	0.46	1.2
CF ₃ CF ₂ H	11.5	3.2	10.1	0.4	0.103	0.28
*CH ₃ CH ₃	8∙4			1.0		

* from ref. (15) in which $E_{CH_4} - E_{C_2H_6} = 2.8 \text{ kcal mole}^{-1}$ (see present text for E_{CH_4}). Activation energies in kcal mole}{-1}; $A_{H}/A_{\sigma}^{\frac{1}{2}}$ in cm² mole $-\frac{1}{2}$ sec $-\frac{1}{2}$.

We conclude that when HFA is photolyzed in the presence of CF₃CH₃, the use of the combination of CF₃ radicals as a reference reaction leads to spurious results. We cannot explain this but further support comes from the fact that for CD₄, values of $E_D - \frac{1}{2}E_c$ and A_D/A_c^{\pm} based on only eqn. (19) are changed by the presence of CF₃CH₃ (see table 2). Accordingly, for all the fluoroethanes, we shall use results obtained by combining eqn. (20) and (21).

The abstraction of H by CF₃ from fluoroethanes was studied by Oksent'vich and Pravednikov ¹⁸ with the following results : CH₃CH₃, (6.5, 2.0×10⁴); CH₃CF₂H, (7.1, 6.4×10³); CF₂HCFH₂, (5.8, 7.2×10²); CF₂HCF₂H, (2.3, 3.8): the first of each pair of figures is $E_{\rm H} - \frac{1}{2}E_c$ in kcal mole⁻¹ and the second figure is $A_{\rm H}/A_c^{\frac{1}{2}}$ in cm^{$\frac{3}{2}$} mole⁻¹ sec⁻¹. These results show such large variations that they must be treated with reserve.

HYDROGEN ABSTRACTION REACTIONS

Activation energies for abstraction of H by CF_3 from fluoroalkanes are summarized in table 4 which also includes data on related reactions.

TABLE 4.—ACTIVATION ENERGIES FOR ABSTRACTION OF H FROM ALKYL HALIDES

$\begin{array}{c} CF_3 + CH_4 \\ + CH_3F \\ + CH_2F_2 \end{array}$	11·2 11·2 11·2	CF ₃ +CH ₃ Cl +CH ₂ Cl ₂ +CHCl ₃	10·6 ª 7·6 6·6	CF ₃ +CH ₃ Br ^b +CH ₃ I	10∙4 7∙5
CH ₃ +CH ₄ ^c +CH ₃ F ^d +CH ₂ F ₂ ^d +CHF ₃ ^e	14·8 11·4 10·2 11·4	$Br+CH_4 f + CH_3F + CH_2F_2 + CH_2F_3$	18·3 15·8 16·3 22·1		
$\begin{array}{c} CF_3+C_2H_6\\+CF_3CH_3\\+CF_2HCF_2H\\+CF_3CF_2H\end{array}$	8·4 13·5 11·9 10·1	$\begin{array}{c} \text{Br} + \text{C}_2\text{H}_6 ^g \\ + \text{CF}_3\text{CH}_3 \\ + \text{CF}_2\text{H}\text{CF}_2\text{H} \\ + \text{CF}_3\text{CF}_2\text{H} \end{array}$	12·3 22·2 18·0 18·0		

a, ref. (2); b, ref. (1); c, ref. (19); d, ref. (20); e, data of Pritchard et al. revised by Coomber and Whittle, ref. (21); f, ref. (6); g, ref. (7). Unless otherwise indicated, each reference gives origin of all data in series. Activation energies in kcal mole⁻¹.

We first consider H abstraction from substituted methanes. Introduction of F or 2F into CH₄ has less effect on H abstraction by CF_3 than does introduction of other halogens. The lack of change of $E_{\rm H}$ along the series CF₃+CH₄, CH₃F, CH₂F₂ is surprising in view of the changes along the corresponding series involving CH₃ radicals. Probably 6 D(C-H) decreases from CH₄ to CH₃F and CH₂F₂ hence the decrease in $E_{\rm H}$ for the reactions involving CH₃ is understandable. The lack of decrease in $E_{\rm H}$ with the corresponding CF₃ reactions suggests that the effect of the decrease in D(C-H) may be fortuitously cancelled by a polar effect which tends to increase $E_{\rm H}$; such an effect was discussed by Whittle and co-workers.⁶ For example, the presence of a fluorine atom reduces the electron density at the hydrogen atoms in CH_3F and hence causes more repulsion between the H attacked and the CF_3 radical since the latter is presumably polarized in the sense $\delta + (\cdot CF_3)\delta - \cdot$. Such a polar effect would be less important in CH_3 reactions hence we suggest that, in the series CH_3 + fluoromethanes, the dominating influence on $E_{\rm H}$ is the decrease in D(C-H). Similarly, for abstraction of H by CF_3 from CH_3X , the polar effect should decrease going from X=F to X=I and indeed $E_{\rm H}$ falls progressively from CH₃F to CH₃I. Again, in the series CF_3 + chloromethanes, we have suggested ³ that the decrease in $E_{\rm H}$ occurs because the decrease in D(C-H) outweighs the polar effect.

With the fluoroethanes, the changes in $E_{\rm H}$ are quite striking. There is a clear parallel between the variations of $E_{\rm H}$ for abstraction of H by CF₃ and by Br; in both cases there is a considerable increase in $E_{\rm H}$ going from CH₃CH₃ to CF₃CH₃ with the hydrogen atoms in the latter being more resistant to attack by Br or CF₃ than in any other compound studied. Coomber and Whittle ⁷ showed that a given C—H is greatly de-activated towards attack by Br if fluorine atoms are attached to an *adjacent* carbon atom whereas if F and H are attached to the *same* carbon atom, there is little effect on the reactivity of the H. Our results on the abstraction of H by CF₃ from fluoromethanes and fluoroethanes show the same phenomenon and can be explained in the same way.

There are also similar changes in A factors for the attack of CF₃ and Br on the fluoroethanes. Thus, from table 3, we obtain the relative values 1.00 : 0.40 : 0.09 for CF₃ abstracting H from CF₃CH₃, CF₂HCF₂H and CF₃CF₂H; for the corresponding abstractions of H by Br,⁷ the A factors are in the ratios, 1.00 : 0.37 : 0.11.

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