Reactions of Trifluoromethyl Radicals with Bromine, Chlorine and Hydrogen Chloride

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Hexafluoroacetone has been photolyzed with HCl and with mixtures of $HCl+Cl_2$, $HCl+Br_2$, Br_2+Cl_2, and Cl_2+HBr. Absolute Arrhenius parameters have been obtained for the reaction,

$$CF_3+HCl \rightarrow CF_3H+Cl \tag{4}$$

using the combination of CF_3 radicals as a reference reaction. The values of A_4 and E_4 have been combined with the results obtained from competitive experiments on the above pairs of reactants and from previous work to give other Arrhenius parameters as follows:

$CF_3+HCl \rightarrow CF_3H+Cl$ $\quad k = 1{\cdot}7\times10^{11} \exp(-5100/RT)$
$CF_3+HBr \rightarrow CF_3H+Br$ $\quad k = 6{\cdot}0\times10^{11} \exp(-2900/RT)$
$CF_3+Cl_2 \rightarrow CF_3Cl+Cl$ $\quad k = 7{\cdot}7\times10^{12} \exp(-3600/RT)$
$CF_3+Br_2 \rightarrow CF_3Br+Br$ $\quad k = 2{\cdot}3\times10^{12} \exp(-700/RT)$
$CF_3+I_2 \rightarrow CF_3I+I$ $\quad k = 2{\cdot}6\times10^{12} \exp(0/RT)$
units; $cm^3\ mole^{-1}\ sec^{-1}$

A study of the reactions

$$Br+CF_3H \rightleftharpoons HBr+CF_3 \tag{1, −1}$$

is important in the determination of the bond dissociation energy $D(CF_3—H)$. To obtain information on reaction (−1), Tucker and Whittle [1] studied the competitive reactions of CF_3 radicals with HBr, I_2 and Br_2,

$$CF_3+I_2 \rightarrow CF_3I+I \tag{2}$$

$$CF_3+Br_2 \rightarrow CF_3Br+Br. \tag{3}$$

Reactions (−1), (2) and (3) were described as " fast " because each removes CF_3 radicals from the system so rapidly that the stationary concentration of CF_3 radicals is very low and consequently the amount of C_2F_6 formed is too small to measure. Thus, the combination of CF_3 radicals cannot be used as a reference reaction. The above work yielded ratios of A factors and differences in activation energies but not absolute Arrhenius parameters. We have therefore studied the reactions of CF_3 radicals with HCl and with mixtures of $HCl+Cl_2$ and $HCl+Br_2$ to determine absolute Arrhenius parameters for one of the reactions which could then be used to obtain the Arrhenius parameters of the others. The source of CF_3 radicals was hexafluoroacetone, HFA.

EXPERIMENTAL

HCl gas from a cylinder (I.C.I. Ltd.) was purified by several bulb-to-bulb distillations. Other materials were as described before.[1, 2] Details of apparatus and procedure have been given elsewhere.[2, 3] For the photolyses, a mercury lamp was used with either of the following filters: filter solution A (ref. (2)) or filter B which consisted of 40 ml of a solution of

$NiCl_2$ (89 g/l.) plus 5 ml of a solution of K_2CrO_4 (0·25 g/l.) made up to 500 ml. Either filter solution was used in a silica flask, diam. 10 cm, which acted as a lens to produce an approximately parallel beam of light. With filter B, a Chance OX7 filter was inserted into the beam. The mercury lines transmitted were: filter A, 2967, 3025, 3130 and 3341 Å; filter B, 3025 and 3130 Å. Filter B is more selective than filter A but has a much lower overall transmission.

ANALYSES: After photolysis, the products were condensed in two Ward stills cooled in liquid nitrogen and CO was pumped off and measured. For experiments with HFA+HCl, the stills were next warmed to −145 and −155°C and they were then pumped until all CF_3H, CF_3Cl, C_2F_6 and the large excess of unreacted HCl had been removed. The mixture was analyzed for the first three of these by V.P.C. using an alumina column preceded by a scrubber column of Carbosorb to remove unreacted HCl. With HFA and the other reactants, the procedure was similar but the Ward stills were at −140 and −150°C.

RESULTS

PHOTOLYSIS OF HEXAFLUOROACETONE WITH HCl

Filter A was used. Preliminary blank experiments showed that when the vapours of HFA and HCl were mixed in an i.-r. cell and left for 12 h the spectrum was unchanged even after the mixture was subsequently frozen several times in liquid air. When HFA was photolyzed with HCl, the products included CF_3H, CF_3Cl and C_2F_6. Possible reactions are,

$$CF_3COCF_3 + h\nu \rightarrow 2CF_3 + CO$$

$$CF_3 + HCl \rightarrow CF_3H + Cl \tag{4}$$

$$CF_3 + Cl \rightarrow CF_3Cl \tag{5}$$

$$Cl + Cl + M \rightarrow Cl_2 + M \tag{6}$$

$$CF_3 + Cl_2 \rightarrow CF_3Cl + Cl \tag{7}$$

$$CF_3 + CF_3 \rightarrow C_2F_6. \tag{8}$$

The ratio R_{CF_3Cl}/R_{CF_3H} varied in the range 0·5-0·9 which suggests that some of the Cl atoms produced by reaction (4) disappear by reaction (6) giving Cl_2. If so, the most likely source of CF_3Cl is reaction (7).

Unlike the corresponding photolysis of acetone with HCl,[4] in which C_2H_6 is not formed, reaction (4) is sufficiently slow for the stationary concentration of CF_3 radicals to be large enough for C_2F_6 to be formed. If CF_3H and C_2F_6 are formed only by reactions (4) and (8) then,

$$k_4/k_8^{\frac{1}{2}} = R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}[HCl]. \tag{9}$$

In order to test eqn. (9), mixtures of HFA+HCl were photolyzed in the temperature range 20-205°C. Two series of experiments were done, each with a constant concentration of HCl equivalent to ~13 mm at 20°C for one series and ~42 mm at 20°C for the other. The amount of HCl reacted was always less than 4 %. An Arrhenius plot for both series is shown in fig. 1; the values of $k_4/k_8^{\frac{1}{2}}$ are independent of the HCl concentration and confirm the validity of eqn. (9). A least-squares treatment of all the data gives

$$k_4/k_8^{\frac{1}{2}} = (3{\cdot}47 \pm 0{\cdot}44) \times 10^4 \exp -(5{,}070 \pm 90)/RT \text{ cm}^{\frac{3}{2}} \text{ mole}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}. \tag{10}$$

PHOTOLYSIS OF HEXAFLUOROACETONE WITH HCl+Cl_2

It is impossible to photolyze HFA without photolyzing Cl_2. However, the latter process is minimized if filter B is used. In fact, the results of these runs were found to be independent of whether filter A or B was used. Tucker and Whittle [2] showed that there is no reaction between HFA and Cl_2 in the absence of photolysis.

When HFA was photolyzed with a mixture of $HCl+Cl_2$, the volatile products were CO, CF_3H and CF_3Cl; no C_2F_6 was detected. If CF_3H and CF_3Cl are formed only by reactions (4) and (7) respectively, then,

$$k_7/k_4 = R_{CF_3Cl}[HCl]/R_{CF_3H}[Cl_2]. \qquad (11)$$

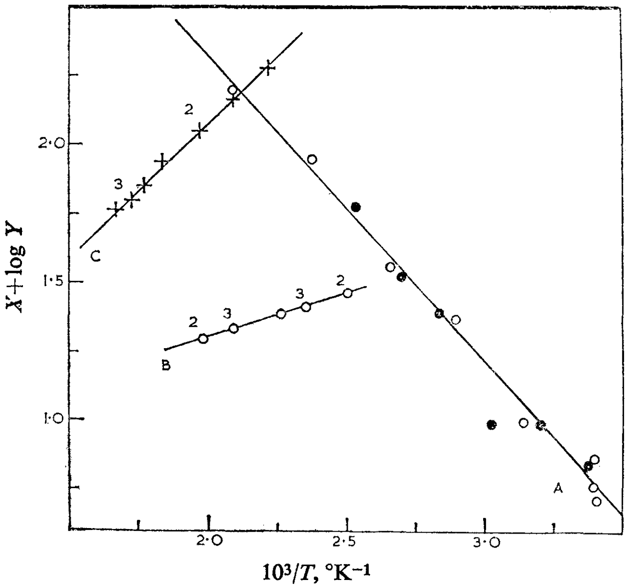

FIG. 1.—Arrhenius plots.

Curve A: reaction of CF_3 with HCl. $X = 0$, $Y = k_4/k_8^{\frac{1}{2}}$. Two series of runs, each at constant HCl concentration equivalent to (i)~13 mm at 20°C, ○ ; (ii) ~42 mm at 20°C, ●.
Curve B: reaction of CF_3 with $HCl+Cl_2$. $X = -1$, $Y = k_7/k_4$.
Curve C: reaction of CF_3 with $HCl+Br_2$. $X = -1$, $Y = k_{13}/k_4$. (A number by a given point indicates the number of runs done at that temperature).

However, CF_3Cl may also be formed by reaction (5). It seems unlikely that this reaction will make a significant contribution relative to reaction (7) since the stationary concentration of Cl atoms is much lower than that of Cl_2 but, in view of the possibility, we have tested eqn. (11) at 126, 152, 205 and 232°C to see if the ratio k_7/k_4 is independent of the ratio $[HCl]/[Cl_2]$. The pressures of HFA and Cl_2 were held constant at ~20 and ~5 mm respectively and the HCl pressure was varied in the range 80-400 mm. If eqn. (11) is valid, a plot of R_{CF_3H}/R_{CF_3Cl} against $[HCl]/[Cl_2]$ will be a straight line of slope k_4/k_7. Such plots are shown in fig. 2 and they fully confirm eqn. (11). In these experiments, it was necessary to use a large excess of HCl over Cl_2 because reaction (4) is much slower than reaction (7). This means that the percentage decomposition of HCl was negligible but the Cl_2 decomposed was in the range 2-8·5 %. Accordingly, the average Cl_2 pressure for any given run was used in eqn. (11), (the initial Cl_2 pressure was known and the final Cl_2 pressure was calculated from the amounts of products assuming that Cl atoms disappear only by reaction (6)).

The results in fig. 2 plus one extra run at 169°C are combined in the Arrhenius plot shown in fig. 1. From it, we have

$$k_7/k_4 = (44{\cdot}5 \pm 1{\cdot}1) \exp(1{,}490 \pm 20)/RT. \qquad (12)$$

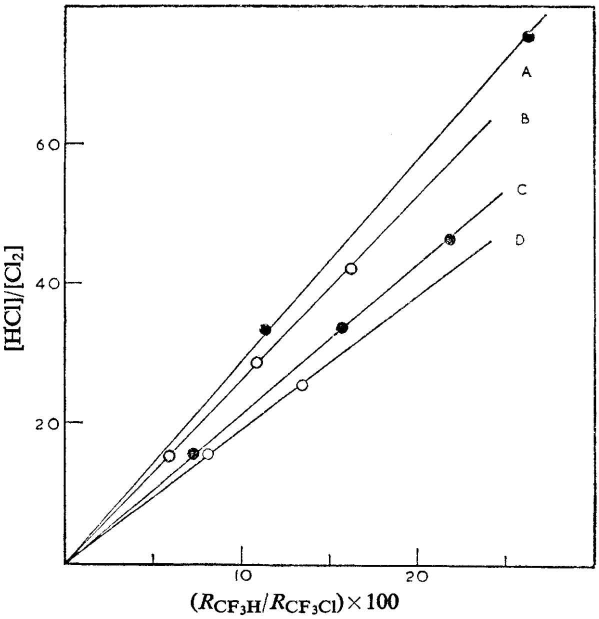

FIG. 2.—Tests of reliability of k_7/k_4 calculated from eqn. (11).
Curve A, 126°; B, 152°; C, 205°; D, 235°C.

PHOTOLYSIS OF HEXAFLUOROACETONE WITH $HCl+Br_2$

Filter B was used so that HFA but not Br_2 was photolyzed.[2] In addition to reaction (4), we have

$$CF_3+Br_2 \rightarrow CF_3Br+Br. \qquad (13)$$

The volatile products were CO, CF_3H, CF_3Cl and CF_3Br, all of which were determined quantitatively. In contrast to the previous section, the presence of CF_3Cl, possibly formed by reaction (5), or more likely reactions (6) and (7), introduces no complications. If CF_3H and CF_3Br are formed only by reactions (4) and (13), then,

$$k_{13}/k_4 = R_{CF_3Br}[HCl]/R_{CF_3H}[Br_2]. \qquad (14)$$

This equation would be invalid if the reaction

$$Br_2+2HCl \rightarrow 2HBr+Cl_2$$

occurred to a significant extent. This is not so because, over our temperature range, the equilibrium constant of this reaction varies from $\sim 5\times 10^{-10}$ to 10^{-7}.

Eqn. (14) has been checked by varying the ratio $[HCl]/[Br_2]$ but there are experimental difficulties here. At 178°, $k_{13}/k_4 \sim 2000$ and the ratio is still larger at lower temperatures, consequently below 178°C, the CF_3H is too small to measure accurately. We have therefore used the range 178-327°C. In fig. 3 are shown plots of R_{CF_3H}/R_{CF_3Br} against $[HCl]/[Br_2]$ at 233 and 306°C; the fact that these are straight lines passing through the origin confirms eqn. (14). The ratio $[HCl]/[Br_2]$ can be varied over only a limited range because the ratio k_{13}/k_4 is so large. For suitable competition over a range of temperatures, it was necessary to use pressures of HCl and Br_2 of $\sim$400 mm and 3·5 mm respectively. It was also necessary to decompose 5-10 % of the Br_2 to obtain enough CF_3Br to analyze, hence the average concentration of Br_2 was used in eqn. (14). The product ratios R_{CF_3Br}/R_{CF_3Cl} and R_{CF_3H}/R_{CF_3Cl} were usually in the ranges 20-50 and 2-5 respectively which suggests that most of the Cl atoms formed by reaction (4) did not react with CF_3 but either combined to form Cl_2 or reacted with Br_2 to give ClBr. An Arrhenius plot of k_{13}/k_4 over the range 178-327°C is shown in fig. 1 ; this includes the data of fig. 3 together with other results. From fig. 1, we have

$$k_{13}/k_4 = (13{\cdot}8 \pm 1{\cdot}8) \exp (4{,}400 \pm 80)/\boldsymbol{RT}. \qquad (16)$$

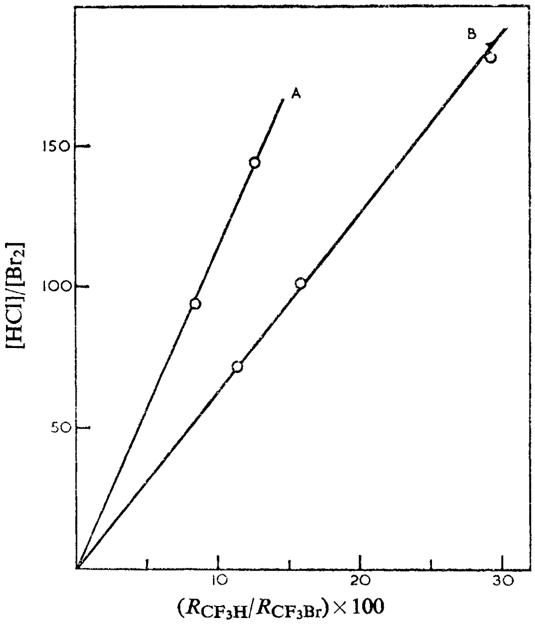

FIG. 3.—Tests of reliability of k_{13}/k_4 calculated from eqn. (14).
Curve A, 232° ; B, 306°C.

PHOTOLYSIS OF HEXAFLUOROACETONE WITH Br_2+Cl_2

From the previous sections on the reactions of CF_3 radicals with $HCl+Cl_2$ and $HCl+Br_2$ (see eqn. (12) and (16)), we calculate that,

$$k_7/k_{13} = (k_7/k_4)/(k_{13}/k_4) = (3{\cdot}22 \pm 0{\cdot}42) \exp - (2{,}910 \pm 90)/\boldsymbol{RT}. \qquad (17)$$

In principle, this result can be checked directly by photolyzing HFA with Br_2+Cl_2. If CF_3Br and CF_3Cl are formed only by reactions (13) and (7), then

$$k_7/k_{13} = R_{CF_3Cl}[Br_2]/R_{CF_3Br}[Cl_2]. \qquad (18)$$

Mixtures of about 40 mm HFA, 6 mm Cl_2 and 6 mm Br_2 were photolyzed in the range 28-190°C, using filter B. The only volatile products were CO, CF_3Cl and CF_3Br. An Arrhenius plot gave

$$k_7/k_{13} = (0{\cdot}69 \pm 0{\cdot}08) \exp - (1{,}930 \pm 80)/\boldsymbol{RT}. \qquad (19)$$

The agreement between this result and that of eqn. (17) is not good. However, the system $HFA+Br_2+Cl_2$ has complications. HFA is best photolyzed with light of the longest possible wavelength to minimize both photosensitization processes and production of hot radicals. This means using the 3130 Å Hg line which also photolyzes Cl_2 so the equilibrium

$$Br_2 + Cl_2 \rightleftharpoons 2ClBr \qquad (20)$$

may be attained. In that case, any of the following reactions could occur,

$$CF_3+Cl_2 \rightarrow CF_3Cl+Cl \qquad (7)$$

$$CF_3+ClBr \begin{array}{l} \nearrow CF_3Cl+Br \qquad (21) \\ \searrow CF_3Br+Cl \qquad (22) \end{array}$$

$$CF_3+Br_2 \rightarrow CF_3Br+Br. \qquad (13)$$

If reactions (21) and (22) occur to a significant extent, eqn. (18) will no longer apply. Reaction (21) is about 14 kcal mole^{-1} more exothermic than reaction (22), consequently the latter is probably much the slower and we shall therefore neglect it. We expect, however, that $E_{21} < E_7$ since D(Cl—Br) is about 6 kcal mole^{-1} less than D(Cl—Cl); thus reaction (21) may be an important source of CF_3Cl. A comparison of eqn. (17) and (19) shows that the respective values of k_7/k_{13} differ by a factor of ~ 3 at 25°C and $\sim 1{\cdot}3$ at 190°C, i.e., the discrepancy decreases as the temperature rises. It is known [5] that K_{20} is virtually independent of temperature and therefore so is the ratio $[ClBr]/[Cl_2]$ for any given mixture of Cl_2+Br_2+ClBr at equilibrium. Now E_7 should be greater than E_{21} so that, as the temperature rises, k_7 increases faster than k_{21} and thus reaction (21) becomes relatively less important than reaction (7). This would explain the better agreement between eqn. (17) and (19) at higher temperatures. It is possible to modify eqn. (18) so that it includes a contribution from reaction (21) but this is hardly justified since we are uncertain whether reaction (20) has actually reached equilibrium. In view of these complications in the system $HFA+Cl_2+Br_2$, we prefer to accept the indirect results given in eqn. (17).

PHOTOLYSIS OF HEXAFLUOROACETONE WITH $HBr+Cl_2$

The results given in eqn. (17) can be checked, in principle, by photolyzing HFA with the pairs of reactants Br_2+HBr and Cl_2+HBr. The first pair was successfully studied by Tucker and Whittle [1] and we have studied the second pair. A mixture of 18 mm HFA, 7·4 mm Cl_2 and 66 mm HBr was photolyzed at 123°C and gave the following amounts of products in micromoles: CO, $8{\cdot}3\times10^{-2}$; CF_3H, $2{\cdot}0\times10^{-2}$; CF_3Cl, $0{\cdot}32\times10^{-2}$; CF_3Br, 16×10^{-2}. Thus CF_3Br is the major product. If this were formed only by the reactions

$$CF_3+HBr \rightarrow CF_3H+Br$$

$$CF_3+Br \rightarrow CF_3Br$$

then R_{CF_3Br} must be $\leqslant R_{CF_3H}$. The products also contained both HCl and Br_2 which were presumably produced by

$$Cl_2+2HBr \rightarrow Br_2+2HCl.$$

We have shown above that the equilibrium for this reaction lies well to the right-hand side, consequently the Br_2 produced will scavenge most of the CF_3 radicals. This system therefore cannot be used to check eqn. (17).

DISCUSSION

In this and previous work,[1] the competitive reactions of CF_3 radicals with various halogens and hydrogen halides have been studied. The system HFA+HCl was the only one in which the products included C_2F_6. Now, for the combination of CF_3 radicals, $k_2 = 2{\cdot}3\times10^{13}$ cm^3 mole^{-1} sec^{-1},[6] and $E_8 = 0{\cdot}0\pm0{\cdot}5$ kcal mole^{-1},[7] so that we obtain from eqn. (10),

$$k_4 = k_{HCl} = 1{\cdot}66\times10^{11} \exp(-5100/RT)\ \text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}.$$

We can combine these absolute values of A_{HCl} and E_{HCl} with results obtained by competitive methods for the various pairs of reactants to give absolute values of A and E for all the reactions studied here and previously. The results are given in table 1. We believe that this is the first time that absolute values have been obtained with reasonable precision for the reactions of a radical with halogens and hydrogen halides. The error limits arise mainly from uncertainties in the data on combination of CF_3 radicals. Thus the difference $E_1 - E_2$ and the ratio A_1/A_2 for any pair of reactants are known much more accurately.

TABLE 1.—ARRHENIUS PARAMETERS FOR THE REACTIONS OF CF_3 RADICALS WITH HALOGENS AND HYDROGEN HALIDES

reaction	A	E	ΔH at 298°K
	$cm^3\ mole^{-1}\ sec^{-1}$	kcal mole^{-1}	
$CF_3 + HCl \rightarrow CF_3H + Cl$	$1{\cdot}7 \times 10^{11}$	$5{\cdot}1 \pm 0{\cdot}5$	-3
$+ HBr \rightarrow CF_3H + Br$	$6{\cdot}0 \times 10^{11}$	$2{\cdot}9 \pm 0{\cdot}5$	-18
$+ Cl_2 \rightarrow CF_3Cl + Cl$	$7{\cdot}7 \times 10^{12}$	$3{\cdot}6 \pm 0{\cdot}5$	-24
$+ Br_2 \rightarrow CF_3Br + Br$	$2{\cdot}3 \times 10^{12}$	$0{\cdot}7 \pm 0{\cdot}5$	-21
$+ I_2 \rightarrow CF_3I + I$	$2{\cdot}6 \times 10^{12}$	$0{\cdot}0 \pm 0{\cdot}5$	-18
$+ H_2 \rightarrow CF_3H + H$		9^a	-2
$CH_3 + HCl \rightarrow CH_4 + Cl$		$4{\cdot}4^b$	-1
$+ HBr \rightarrow CH_4 + Br$		$1{\cdot}4^c$	-16

ΔH's are approximate using $D(CF_3—H) = 106{\cdot}2$,[9] $D(CH_3—H) = 103{\cdot}8$ [9] and assuming that $D(CF_3—Cl) \sim D(CH_3—Cl) = 82$ (based on $D(CH_3—H)$ + standard thermodynamic data [13]), $D(CF_3—Br) = 68{\cdot}0$ [12] and $D(CF_3—I) = 54$,[14] all in kcal mole^{-1}.

a, ref. (11), *b*, calculated from ΔH and $E(Cl + CH_4 \rightarrow HCl + CH_3)$, ref. (15). *c*, from ref. (16) assuming $E(CH_3 + I_2 \rightarrow CH_3I + I) = 0$.

The results in table 1 can be partly checked as follows. From previous work,[1] $E_{Br_2} - E_{I_2} = 0{\cdot}8 \pm 0{\cdot}2$ kcal mole^{-1}. It is thought that the reactions of simple radicals with I_2 usually have zero activation energy, hence if $E_{I_2} = 0$, $E_{Br_2} = 0{\cdot}8 \pm 0{\cdot}2$ kcal mole^{-1} which agrees well with the absolute value in the table.

In table 1, we give enthalpy changes for the reactions between CF_3 radicals and halogens or hydrogen halides. Although E increases as the reaction becomes less exothermic, there is no simple quantitative relation between the changes in E and ΔH. Probably the most surprising result is the small difference between $E(CF_3 + HCl)$ and $E(CF_3 + HBr)$ in spite of the large difference in ΔH for the two reactions. It is known [8] that, when CF_3 or CH_3 reacts with a given RH, E_{CF_3} is usually less than E_{CH_3} by about 3 kcal mole^{-1}. Tucker and Whittle [2] showed that HBr is an exception to this rule and we now see from table 1 that HCl is also an exception. Assuming [9] that $D(CH_3—H) = 103{\cdot}8$ kcal mole^{-1} and $D(CF_3—H) = 106{\cdot}2$ kcal mole^{-1}, we have $\Delta H(CH_3 + HCl) = -0{\cdot}8$ kcal mole^{-1} and $\Delta H(CF_3 + HCl) = -3{\cdot}2$ kcal mole^{-1}, yet the reaction between CF_3 and HCl has the higher activation energy. This indicates that polar effects are important in these reactions as suggested by Whittle and coworkers.[2, 10] This is confirmed by the reaction [11]

$$CF_3 + H_2 \rightarrow CF_3H + H$$

which, like $CF_3 + HCl$, is slightly exothermic and yet has a much higher activation energy. Polar effects will be less important in the reaction between CF_3 and H_2.

The activation energies for the reactions of CF_3 with HCl and HBr can be used to calculate $D(CF_3—H)$ and this has been done by Coomber and Whittle.[17] These authors also discuss the A factors in table 1 together with those of the reverse reactions.

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