J. Chem. Soc., Faraday Trans. 1, 1983, 79, 1471-1482

Bromination of Fluoroalkanes

Part 5.—Kinetics of Forward and Reverse Reactions in the System $Br_2+i-C_3F_7H \rightleftharpoons HBr+i-C_3F_7Br$

BY BRIAN S. EVANS,[†] IAN WEEKS[‡] AND ERIC WHITTLE^{*}

Chemistry Department, University College, Cardiff CF1 1XL

Received 8th November, 1982

The kinetics of the forward and reverse reactions in the gas-phase system

$$Br_2+i-C_3F_7H \rightleftharpoons HBr+i-C_3F_7Br$$

have been studied. The slow steps for the forward and reverse reactions, respectively, are

$$Br + i - C_3 F_7 H \rightarrow HBr + i - C_3 F_7$$
(2)

$$Br + i - C_3 F_7 Br \rightarrow Br_2 + i - C_3 F_7.$$
 (-3)

The Arrhenius parameters obtained, for the range 421-534 °C, are

log
$$A_2$$
/cm³ mol⁻¹ s⁻¹ = 12.66 ± 0.34, $E_2 = 81.2 \pm 3.3$

$$\log A_{-3}/\mathrm{cm^3 \ mol^{-1} \ s^{-1}} = 13.80 \pm 0.29, \quad E_{-3} = 86.3 \pm 4.2 \ \mathrm{kJ \ mol^{-1}}$$

The competitive brominations of mixtures of $i-C_3F_7H + C_2F_5H$ and $i-C_3F_7H + n-C_3F_7H$ have been studied over the ranges 249–430 and 220–402 °C, respectively. Each system yielded Arrhenius parameters for reaction (2) which are in excellent agreement with those given above. The results lead to the following bond dissociation energies at 298 K:

$$D(i-C_3F_7-H) = 433.3 \pm 2.4 \text{ kJ mol}^{-1}, D(i-C_3F_7-Br) = 273.8 \pm 4.7 \text{ kJ mol}^{-1}.$$

Attempts were made to measure $D[(CF_3)_3C-H]$ using competitive photobromination and photochlorination. However, $(CF_3)_3C-H$ is so unreactive that only the approximate result $D[(CF_3)_3C-H] \approx 456$ kJ mol⁻¹ was obtained. The trends in C-H and C-Br bond dissociation energies are compared in alkanes, fluoroalkanes and the corresponding bromides.

It is well known that there is a progressive decrease in C—H bond dissociation energy along the series Me—H, Et—H, i-Pr—H and t-Bu—H. The trend could well be different for the analogous series involving perfluoroalkyl groups R_F . However, values of $D(R_F$ —H) are known only for CF_3 —H¹ and C_2F_5 —H.² We now describe the first determination of $D(R_F$ —H) for the third member of the series, i- C_3F_7 —H. This involves a study of the kinetics of the overall forward reaction,

$$Br_2 + i - C_3 F_7 H \rightleftharpoons HBr + i - C_3 F_7 Br.$$
 (1, -1)

The kinetics of the overall reverse reaction (-1) were also studied and a value of $D(i-C_3F_7-Br)$ was obtained.

The value of $D(i-C_3F_7-H)$ was checked by means of competitive brominations of mixtures of $i-C_3F_7H+C_2F_5H$ and $i-C_3F_7H+n-C_3F_7H$.

[†] Present address: Department of Science, Stockport College, Wellington Road South, Stockport, Cheshire.

[‡] Present address: Department of Medical Biochemistry, Welsh National School of Medicine, Heath Park, Cardiff CF4 4XN.

1472

BROMINATION OF FLUOROALKANES

We also describe the results of attempts to measure $D(R_F - H)$ where $R_F = per-fluoro-t-butyl$. An approximate value of $D[(CF_3)_3C - H]$ was obtained.

EXPERIMENTAL

MATERIALS

The sources of, or preparations of, Br_2 , HBr, C_2F_5H and $n-C_3F_7H$ were as in ref. (3)–(5). i- C_3F_7H was made by photolysis of i- C_3F_7I (Peninsular ChemResearch) in the presence of $(CH_3)_2CHCH(CH_3)_2$ or $HBr.^6 C_2F_5Br$ and $n-C_3F_7Br$ were made by photolysing a large excess of Br_2 with C_2F_5H or $n-C_3F_7H$ in our reaction vessel at 200 °C. i- C_3F_7Br was similarly made by photolysis of excess Br_2 with i- C_3F_7I at 200 °C. The products were freed of halogens and HBr by passage through Carbosorb followed by auramine on brick dust. Middle fractions from bulb-to-bulb distillations (-80 to -196 °C) were pure, as indicated by infrared spectroscopy and gas chromatography.

APPARATUS AND PROCEDURE

The apparatus was essentially as described in ref. (1). The progress of the thermal reactions (1) and (-1) was monitored by following the decay of Br₂ in forward reactions and the growth in back reactions. Product mixtures were analysed for i-C₃F₇H and i-C₃F₇Br by gas chromatography using a 5.8 m column of 15% silicone oil (MS200) on Chromosorb P preceeded by a halogen scrubber of auramine on brick dust, both at 0 °C.

In the competitive experiments, mixtures of reactants were irradiated with light from a 250 W Osram medium-pressure mercury lamp. A parallel beam passed through a cobalt-glass filter whose transmission roughly matched the Br_2 absorption spectrum. Details of analysis of products are given later.

RESULTS

1. THERMAL BROMINATION OF $i-C_3F_7H$

The overall thermal bromination of $i-C_3F_7H$ should be described by reaction (1)

$$Br_2 + i - C_3 F_7 H \rightleftharpoons HBr + i - C_3 F_7 Br.$$
 (1, -1)

In agreement with this, we found no species other than those present in reaction (1) when reaction mixtures were left for much longer periods than those used for kinetic measurements. The expected mechanism of reaction (1) involves the steps

$$Br_{2} \rightleftharpoons^{n_{c}} 2Br$$

$$Br + i - C_{3}F_{7}H \rightleftharpoons HBr + i - C_{3}F_{7} \qquad (2, -2)$$

$$i-C_3F_7+Br_2 \rightleftharpoons i-C_3F_7Br+Br.$$
 (3, -3)

In the early stages reaction (-3) can be ignored. If chain termination occurs only by combination of Br atoms, the above mechanism leads to the rate law

$$-\frac{d[Br_2]}{dt} = \frac{k_2 K_c^{\frac{1}{2}} [Br_2]^{\frac{1}{2}} [i-C_3 F_7 H]}{1+k_{-2} [HBr]/k_3 [Br_2]}.$$
 (4)

The initial rate, when negligible HBr is present, is given by

$$-\frac{d[Br_2]}{dt} = k_2 K_c^{\frac{1}{2}} [Br_2]^{\frac{1}{2}} [i - C_3 F_7 H].$$
(5)

Eqn (5) was first checked by performing runs at 444 °C. Initial rates of removal of Br_2 were obtained from the photometer traces by computer curve-fitting. From 6 runs using 33 Torr i- C_3F_7H and varying Br_2 in the range 4–20 Torr, a plot of log (initial rate) against log $[Br_2]$ gave an order in Br_2 of 0.54 ± 0.04 . Similarly, from 7 runs with

17 Torr Br_2 and varying i- C_3F_7H in the range 10–67 Torr, we obtained an order in i- C_3F_7H of 1.07 ± 0.05 . Thus eqn (5) is confirmed. Runs were also done at five other temperatures in the range 421–534 °C. The initial pressures of Br_2 and i- C_3F_7H were varied at each temperature. At any given temperature the value of $k_2K_c^{\frac{1}{2}}$ was independent of these variations. In all, 38 runs were done. Values of K_c were calculated from data in the Janaf tables,⁷ and hence k_2 was obtained from each run. An Arrhenius plot, shown in fig. 1, leads to

$$\log (k_{\rm s}/\rm{cm}^3 \,\rm{mol}^{-1} \,\rm{s}^{-1}) = (12.66 \pm 0.34) - (81\,200 \pm 3300)/\theta \tag{6}$$

where $\theta = 2.303 \ RT \ J \ mol^{-1}$. Error limits are one standard deviation.



Fig. 1. Arrhenius plots. Lower curve, k_2 . Upper curve, k_{-3} . Where several points are close together, the mean value is plotted and the number of runs involved is indicated.

2. THERMAL REACTION BETWEEN $i-C_3F_7Br$ and HBr

The overall reaction (-1) between i-C₃F₇Br and HBr is conveniently initiated by Br atoms, as in reaction (-3). The Br atoms are generated by adding Br₂ to the initial HBr+i-C₃F₇Br mixture. Assuming that Br and Br₂ are in equilibrium, the early stages of reaction (-1) involve steps (3), (-3) and (-2). The resulting rate law is

$$\frac{\mathrm{d}[\mathbf{Br}_{2}]}{\mathrm{d}t} = \frac{k_{-3}K_{\mathrm{c}}^{\dagger}[\mathbf{Br}_{2}]^{\frac{1}{2}}[\mathbf{i}-\mathbf{C}_{3}\mathbf{F}_{7}\mathbf{Br}]}{1+k_{3}[\mathbf{Br}_{2}]/k_{-2}[\mathbf{HBr}]}.$$
(7)

BROMINATION OF FLUOROALKANES

Reaction (2) does not become important until later, when the concentration of $i-C_3F_7H$ becomes substantial.

The measurement of initial rates for the back reaction does not lead to a simpler form of eqn (7), unlike the forward reactions where use of initial rates permitted replacement of eqn (4) by the simpler eqn (5). This is because the back reactions are initiated by adding Br₂ to the HBr+i-C₃F₇Br so that the denominator in eqn (7) is never unity. The determination of k_{-3} using eqn (7) can be made in several ways. For example, a series of runs can be performed at a given temperature using a fixed pressure of i-C₃F₇Br and various ratios of Br₂ to HBr. The results can be introduced into a rearranged form of eqn (7) so that a graphical treatment gives k_{-3} and the ratio k_3/k_{-2} . Alternatively, values of k_3/k_{-2} can be obtained by studying the inhibiting effect of HBr on the overall *forward* reaction and then applying eqn (4). The values of k_3/k_{-2} so obtained are then introduced into eqn (6), which can thus be applied directly to the kinetic results on the back reaction to give k_{-3} . However, there is a third and better way of obtaining k_3/k_{-2} , as follows.

Evans and Whittle² have described an independent way of measuring ratios of rate constants, such as k_3/k_{-2} . Weeks and Whittle⁸ have applied their technique to reactions (3) and (-2). This involves photolysis of Br₂ in the presence of a mixture of HBr+i-C₃F₇I so that i-C₃F₇ radicals are produced by the reaction

$$Br+i-C_3F_7I \rightarrow IBr+i-C_3F_7$$
.

The radicals then react competitively with HBr and Br_2 by reactions (-2) and (3), respectively. This work yielded

$$\log k_3 / k_{-2} = (0.55 \pm 0.07) + (10900 \pm 600) / \theta.$$
(8)

Eqn (8) was used to find k_3/k_{-2} at each temperature at which a back reaction was carried out. The result, together with the appropriate initial rate and concentrations of reactants, was introduced into eqn (7) and so k_{-3} was obtained. 14 runs were done at 5 temperatures in the range 421-534 °C. At each temperature substantial changes in reactant concentrations were made, but the values of k_{-3} from eqn (7) were constant within experimental error. An Arrhenius plot is shown in fig. 1, from which

$$\log \left(k_{-3} / \text{cm}^3 \,\text{mol}^{-1} \,\text{s}^{-1} \right) = (13.80 \pm 0.29) - (86300 \pm 4200) / \theta. \tag{9}$$

3. BROMINATION OF MIXTURES OF $i-C_3F_7H+C_2F_5H$

If a mixture of $Br_2 + i - C_3F_7H + C_2F_5H$ is irradiated in the vapour phase with blue light, the expected reactions are (2), (3) and

$$Br_2 + h\nu \to 2 \text{ Br}$$

$$Br + C_2F_5H \to HBr + C_2F_5 \tag{10}$$

$$C_2F_5 + Br_2 \rightarrow C_2F_5Br + Br \tag{11}$$

$$Br + Br + M \rightarrow Br_2 + M$$
.

If reactions (3) and (11) are the only sources of $i-C_3F_7Br$ and C_2F_5Br , respectively, then

$$\beta = \frac{R(i-C_3F_7Br)}{R(C_2F_5Br)} = \frac{k_2[i-C_3F_7H]}{k_{10}[C_2F_5H]}$$
(12)

where R denotes rate of formation. Eqn (12) should apply irrespective of how Br atoms are formed.

Mixtures of reactants were admitted to the reaction vessel in the order i- C_3F_7H , C_2F_5H , Br_2 . The temperature range used was 249–430 °C. At all but the highest temperature ($T \le 401$ °C) there was no dark reaction. At 430 °C a slow thermal bromination began as soon as Br_2 was added. This did not affect the results as only short photolysis times were needed at 430 °C.

If eqn (12) is valid, the ratio of the rates of formation of products, denoted by β , should be independent of photolysis time. To check this, samples were removed from each run after various photolysis times and were analysed by gas-solid chromatography (g.s.c.). The values of β were independent of photolysis time. This is rare for competitive brominations and occurs because k_2 and k_{10} differ by less than a factor of 2. Hence the right-hand side of eqn (12) does not begin to change significantly until substantial conversions of i-C₃F₇H and C₂F₅H have occurred.

	<i>p</i> /Torr			[i-C ₃ F ₇ H] _i	k,	
<i>T/</i> °C	Br ₂	i-C ₃ F ₇ H	C_2F_5H	$\frac{[C_2F_5H]_i}{[C_2F_5H]_i}$	$\frac{1}{k_{10}}$	
249.4	12.7	20.8	20.8	0.999	0.542	
249.4	12.6	20.8	21.2	0.981	0.607	
249.4	17.8	41.6	10.2	4.08	0.615	
299.1	18.8	21.0	20.9	1.01	0.516	
299.1	18.7	41.3	10.6	3.90	0.709	
351.5	19.1	21.2	20.6	1.03	0.572	
351.2	19.3	20.7	20.9	0.990	0.598	
351.5	8.5	41.9	20.6	2.03	0.639	
351.5	19.3	41.6	10.5	3.98	0.636	
351.2	39.0	20.9	20.8	1.00	0.617	
400.9	18.2	21.3	20.6	1.04	0.594	
400.9	17.9	42.1	10.3	4.07	0.707	
400.9	7.9	20.9	20.7	1.01	0.583	
430.0	19.7	21.2	22.2	0.956	0.676	

Table 1	۱. (Competitive	results f	or	the	system	$Br_{2} +$	-i-C	$_{3}F_{7}$	H +	C,F	H,
		1										

The analysis of the product mixtures by g.s.c. presented difficulties. The column consisted of 40 cm of activated alumina preceded by 35 cm of auramine on brick dust to remove $Br_2 + HBr$. The column was at room temperature. The alumina was rapidly deactivated and needed renewal each day. Samples of a standard calibration mixture of $i-C_3F_7Br+C_2F_5Br$ were injected between run samples to determine sensitivities.

Runs were done at five temperatures in the range 249–430 °C. For each run, the mean value of β was introduced into eqn (12) and the ratio k_2/k_{10} was calculated. The results are given in table 1. At any given temperature k_2/k_{10} is independent of the initial ratio [i-C₃F₇H]/[C₂F₅H] and of the initial pressure of Br₂. This confirms that eqn (12) is valid. An Arrhenius plot of the data is shown in fig. 2. A least-squares analysis gives

$$\log k_2 / k_{10} = -(0.08 \pm 0.10) - (1530 \pm 1210) / \theta.$$
(13)

4. BROMINATION OF MIXTURES OF $i-C_3F_7H + n-C_3F_7H$

The mechanism of bromination of $i-C_3F_7H + n-C_3F_7H$ should be similar to that of the previous section except that reaction (10) will be replaced by

 $Br + n - C_3 F_7 H \rightarrow HBr + n - C_3 F_7$ (14)



Fig. 2. Arrhenius plots for competitive results. Lower curve, X = 0.9, $k_a/k_b = k_2/k_{14}$. Upper curve, X = 1, $k_a/k_b = k_2/k_{10}$. Numbers by points have the same meaning as in fig. 1.

with n-C₃F₇ radicals being removed by reaction with Br₂. The analogue of eqn (12) is $R(I_{-}C \in Br) = k [i_{-}C \in H]$

$$\frac{R(I-C_3F_7Br)}{R(n-C_3F_7Br)} = \frac{k_2[I-C_3F_7H]}{k_{14}[n-C_3F_7H]}.$$
(15)

The experimental procedure was essentially as in the previous section with photobromination of mixtures of $Br_2+i-C_3F_7H+n-C_3F_7H$. However, we could not find a gas-chromatography column which would satisfactorily separate all four components in the product mixture so analyses were done by i.r. spectroscopy. The ratio [i-C_3F_7Br]/[n-C_3F_7Br] was determined using the 969 cm⁻¹ band of i-C_3F_7Br and the 847 cm⁻¹ band of n-C_3F_7Br. The latter band was partly overlapped by the 861 cm⁻¹ band of i-C_3F_7H and, to a lesser extent, by the 835 cm⁻¹ band of n-C_3F_7H. This was allowed for as follows.

Two i.r. gas cells were mounted in the sample and reference beams of an i.r. spectrometer and both were connected independently to the vacuum line. Beer's-law plots were constructed for both i-C₃F₇Br (969 cm⁻¹) and n-C₃F₇Br (847 cm⁻¹), with the reference cell evacuated. These plots were checked frequently. A run mixture was photolysed for a suitable time and then the contents of the reaction vessel were frozen into the sample cell. Preliminary experiments showed that the Br, in the mixture slowly disappeared, probably by reaction with the picein wax used to seal the NaCl windows on to the i.r. cell. Each reaction mixture was therefore freed from Br₂ and HBr by passing it through a tube of auramine on brick dust before it entered the i.r. gas cell. Blank experiments, with and without this scrubbing, showed that scrubbing did not affect the ratio of bromides. Once the reaction mixture was in the sample cell the i.r. spectrometer was set to the 1037 cm⁻¹ band of $n-C_3F_7H$, and $n-C_3F_7H$ was then admitted to the reference cell until the absorption was nulled. The spectrometer was then set to the 861 cm⁻¹ band of $i-C_3F_7H$ and $i-C_3F_7H$ was added to the reference cell until the absorption by i- C_3F_7H in the sample cell was cancelled. The spectrum of the products was then scanned to obtain the absorbances needed at 969 and 847 cm^{-1} .

Runs were done in the range 220-402 °C. The whole of the products of each run were needed for each analysis, so periodic sampling after different photolysis times, as in the previous section, was not done. However, photolysis times were varied in

B. S. EVANS, I. WEEKS AND E. WHITTLE 1477

separate runs so that the percentage conversion of the more reactive compound $(n-C_3F_7H)$ fell in the range 8-31%. The ratio k_2/k_{14} , obtained using eqn (15), was unaffected at a given temperature. This is expected, since $k_2/k_{14} \approx 2$ so that the ratio $[i-C_3F_7H]/[n-C_3F_7H]$ changes little during the photolysis times used. At each temperature the ratio of reactants was varied but this did not effect the calculated value of k_2/k_{14} . The results were also independent of the order of admission of the reactants to the reaction vessel. In certain runs duplicate analyses were made by dividing the product mixture into two equal samples. Reproducibility was excellent. One experiment at the highest temperature was carried out without photolysis. The percentage conversion in the dark after 158 min was the same as that after a 40 s photolysis. Hence the thermal reaction can be neglected.

		<i>p</i> /Torr	[i-C ₂ F-H]	k.	
T∕°C	Br ₂	i-C ₃ F ₇ H	n-C ₃ F ₇ H	$\frac{1}{\left[n-C_{3}F_{7}H\right]_{i}}$	$\frac{1}{k_{14}}$
219.6	9.0	20.8	20.5	1.01	0.375
219.5	8.7	20.7	20.6	1.00	0.438
255.8	10.0	20.3	19.1	1.06	0.442
256.3	10.6	41.4	9.0	4.60	0.442
256.1	13.8	51.6	5.3	9.68	0.430
256.1	21.1	20.3	19.2	1.06	0.467
299.9	10.6	20.6	19.3	1.06	0.463
299.4	10.5	20.6	19.5	1.06	0.472
300.2	8.8	41.4	10.7	3.88	0.411
349.8	10.6	20.8	19.4	1.08	0.519
350.3	5.3	20.3	19.5	1.04	0.496
350.3	10.5	10.4	19.4	0.537	0.475
349.8	10.9	20.5	9.1	2.25	0.464
350.6	11.0	41.5	8.7	4.78	0.466
350.6	11.1	41.3	3.7	11.3	0.446
400.6	8.2	20.7	20.3	1.02	0.523
401.3	8.0	41.7	10.3	4.06	0.474
401.6	8.3	20.7	20.1	1.03	0.499

Table 2. Competitive results for the system $Br_2 + i-C_3F_7H + n-C_3F_7H$

The experimental results are given in table 2. An Arrhenius plot of k_2/k_{14} is shown in fig. 2. By a least-squares analysis

$$\log k_2 / k_{14} = -(0.09 \pm 0.05) - (2750 \pm 560) / \theta.$$
⁽¹⁶⁾

A comparison of the results in eqn (13) and (16) shows that the standard deviations were less using i.r. analysis than when using g.s.c. analysis.

The competitive data in eqn (13) and (16) can be used to obtain absolute values of A_2 and E_2 as follows. Whittle and coworkers^{3, 4} studied the competitive brominations of several fluoromethanes, fluoroethanes and n-C₃F₇H. Various cross-checks were applied and the data were shown to be internally consistent. The results were re-evaluated by Amphlett and Whittle¹ using new absolute A and E values for BR+CF₃H and Br+C₂F₅H. They recommended the Arrhenius parameters for reactions (10) (Br+C₂F₅H) and (14) (Br+n-C₃F₇H) which are given below in table 3.

BROMINATION OF FLUOROALKANES

These values can be combined with our present results in eqn (13) and (16), respectively, to give the following Arrhenius parameters for reaction (2).

source	$\log (A_2/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E_2/\mathrm{kJ}~\mathrm{mol}^{-1}$
C_2F_5H as reference and eqn (13)	12.95 ± 0.10	82.30 ± 1.24
$n-C_3F_7H$ as reference and eqn (16)	12.86 ± 0.11	82.56 ± 0.81 .

This excellent agreement supports the various Arrhenius parameters assigned previously¹ and also suggests that the values of A_2 and E_2 from the two sets of results above should be reliable.

5. ATTEMPTS TO DETERMINE THE BOND DISSOCIATION ENERGY $D[(CF_3)_3C-H]$

The magnitude of $D[(CF_3)_3C-H]$ is of particular interest since no bond dissociation energy is known for any compound containing the $(CF_3)_3C-$ group. Furthermore, nothing is known about the reactivity of $(CF_3)_3C$ radicals and little is known about the reactivity of compounds of the type $(CF_3)_3C-X$ where X = H or a halogen.

Preparation of $(CF_3)_3CH$ was difficult. We used the method of Knunyants and coworkers⁹ in which $(CF_3)_2C=CF_2$ is reacted with water in the presence of triethylamine. Our results differed considerably from those of Knunyants, but $(CF_3)_3CH$ was eventually made using a modification of the synthesis.⁸ Its identity was confirmed by i.r. and n.m.r. spectra.

We first tried to measure $D[(CF_3)_3C - H]$ by determining the activation energy of the reaction $Br + (CF_3) C + HBr + (CF_3) C$ (17)

$$Br + (CF_3)_3 CH \rightarrow HBr + (CF_3)_3 C.$$
(17)

It should be possible to find A_{17} and E_{17} by a competitive method, as in the previous two sections, provided that a suitable competitor can be found. If $(CF_3)_3CH$ had a weak C-H bond, as does (CH₃)₃C-H, it should be readily brominated. In a preliminary experiment 20 Torr of (CF₃)₃CH was mixed with 60 Torr of Br₂ at 360 °C and irradiated with the unfiltered light from the Hg lamp used in the first part of this paper. Over several hours a little Br₂ was consumed and three small product peaks were obtained using g.l.c. analysis. One of these was probably $(CF_a)_a CBr$. The mixture was left in the dark for a further 60 h. Little further Br_2 was used up and the peak assigned to $(CF_a)_3CBr$ hardly changed. The products showed a strong i.r. absorption at ca. 1850 cm⁻¹ which suggests that a fluoro-olefin was present. The i.r. spectrum also indicated the presence of SiF₄. These observations indicate the following points. (i) $(CF_3)_3CH$ is exceptionally resistant to bromination. Under the same conditions $i-C_3F_7H$ would have been readily brominated yet that compound is itself resistant to bromination. (ii) $(CF_{3})_{3}CH$ was brominated so slowly that there was time for pyrolysis to occur, giving $(CF_3)_2C=CF_2+HF$. The HF would react with the silica reaction vessel to give SiF₄. The bromination of $(CF_3)_3CH$ is so slow relative to the pyrolysis that it will probably be impossible to study the competitive bromination of $(CF_3)_3CH$ even if a suitable competitor can be found.

In view of these complications we turned to photochlorinations, which involve much lower activation energies than photobrominations. Hence it should be possible to use lower temperatures and avoid thermal decomposition of $(CF_3)_3$ CH. Also, Cl atoms are less selective than Br atoms, so in principle a wider range of competitors is available.

If a mixture of $(CF_3)_3CH + RH + Cl_2$ is photolysed, the Cl atoms should react as follows $Cl + (CF_2)_2CH \rightarrow HCl + (CF_2)_2C$ (18)

$$Cl + (CF_3)_3 CH \to HCl + (CF_3)_3 C$$
⁽¹⁸⁾

$$Cl + RH \rightarrow HCl + R.$$
 (19)

If all $(CF_3)_3C$ and R radicals react with Cl_2 to give the corresponding chlorides (*i.e.* if termination steps involving these radicals are unimportant) then

$$\frac{R\{(CF_3)_3CCl\}}{R(RCl)} = \frac{k_{18}[(CF_3)_3CH]}{k_{19}[RH]}.$$
(20)

Determination of the ratio of chlorides on the left-hand side of eqn (20) would permit calculation of k_{18}/k_{19} and hence of k_{18} if k_{19} were known.

Our first experiment involved photolysis at 240 °C of Cl_2 with a mixture of $(CF_3)_3CH$ and $i-C_3F_7H$ in the ratio 22:1. Two products were detected with g.l.c. retention times identical to those of $(CF_3)_3CCl$ and $i-C_3F_7Cl$, respectively. [Impure samples of the chlorides had been made by photolysis of separate mixtures of $Cl_2 + (CF_3)_3CH$ and $Cl_2 + i-C_3F_7H$.] The g.l.c. sensitivities of the chlorides were estimated, so the ratio of the chlorides needed for eqn (20) could be found. This led to $k_{18}/k_{19} \approx 1/200$, which corresponds to an activation energy difference $E_{18} - E_{19} \approx 23$ kJ mol⁻¹, assuming $A_{18} = A_{19}$.

It is evident that $(CF_3)_3CH$ is exceptionally resistant to both photobromination and photochlorination. Other competitive photochlorinations were carried out using $(CF_3)_3CH + CF_3H$. However, we were unable to achieve a satisfactory g.l.c. separation of CF_3H , CF_3Cl and $(CF_3)_3CCl$. An alternative competitior, CF_3CH_3 , was unsuitable, as the primary product, CF_3CH_2Cl , undergoes rapid secondary chlorination to CF_3CHCl_2 and CF_3CCl_3 . The above competitiors were chosen for their resistance to chlorination. Most other compounds are unsuitable as they are chlorinated so much faster than $(CF_3)_3CH$ that negligible $(CF_3)_3CCl$ would be formed.

It is clear that determination of $D[(CF_3)_3C-H]$ using halogenation methods will be extremely difficult. The inertness of $(CF_3)_3CH$ to halogenation, relative to compounds such as CF_3H , CF_3CH_3 and $i-C_3F_7H$ which are themselves extremely resistant to halogenation, means that competitive studies require use of a large excess of $(CF_3)_3CH$ over the other competitor in order to get significant yields of $(CF_3)_3CCI$ or $(CF_3)_3CBr$. Yet $(CF_3)_3CH$ is difficult to make in quantity, so the use of a large excess presents problems.

DISCUSSION

ARRHENIUS PARAMETERS FOR BROMINATION REACTIONS

The direct bromination of $i-C_3F_7H$ (section 1) gave the Arrhenius parameters for reaction (2) which are given in eqn (6). The competitive studies (sections 3 and 4) gave two further independent sets of values A_2 and E_2 . Since all three sets agree well, we recommend the mean values

$$\log (A_2/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 12.82 \pm 0.12, \quad E_2 = 82.0 \pm 1.2 \text{ kJ mol}^{-1}.$$

These values are compared with related data in table 3. The A factors are virtually constant along the fluoroalkane series and the same is true for the alkane series, although the mean log A for alkanes is slightly greater than for fluoroalkanes. However, the patterns of reactivity with Br atoms along the two series are entirely different.

The fall in E from CH_3 —H to t-Bu—H is well known and is readily explained in terms of a progressive decrease in C—H bond dissociation energy along the series (see table 4 below). Thus CH_4 is the least reactive and $(CH_3)_3CH$ is the most reactive. In contrast, the fluoroalkane series reveals much smaller changes in reactivity. There is little difference in E values for C_2F_5H , $n-C_3F_7H$ and $i-C_3F_7H$, with $i-C_3F_7H$ being the least reactive of the trio, whereas $i-C_3H_7H$ is much the most reactive of the three

RH	$\log A^a$	<i>E</i> ^{<i>b</i>}	ref.	RH	$\log A^a$	Eb	ref.
CF ₃ —H	13.11	93.4	1	CH ₃ —H	13.39	77.7	1
$C_2F_5 - H$	13.03	80.8	1	C,H,H	13.36	57.1	1
$n-C_3F_7-H$	12.95	79.8	1	n-C ₃ H ₂ —H	(13.36)	55.2	đ
i-C ₃ F ₇ —H	12.82	82.0	с	i-C ₃ H ₂ H	13.66	43.5	1
(CF ₃) ₃ C—H		ca. 101	1	(CH ₃) ₃ Ċ—H	13.58	32.5	1

Table 3. Some Arrhenius parameters for reactions of the type $Br + RH \rightarrow HBr + R$

^a Per H-atom abstracted, units cm³ mol⁻¹ s⁻¹. ^b kJ mol⁻¹. ^c Present work. ^d Assuming (i) same A factor for attack of Br on primary H in C₂H₆, C₃H₈ and n-C₄H₁₀ and (ii) same ratio of k (primary)/k(secondary) for C₃H₈ and n-C₄H₁₀. Then use k(secondary)/k(primary) for n-C₄H₁₀ = 82 at 419 K [ref. (17)] together with Arrhenius parameters for attack of Br on s-H in n-C₄H₁₀ [ref. (1) and (18)].

corresponding alkanes. The most striking difference is between $(CH_3)_3CH$, the most reactive alkane, and $(CF_3)_3CH$, the least reactive of the fluoroalkanes.

The reactivity of the fluoroalkanes appears to follow the changes in D(C-H) along the series. These are discussed in the following section.

BOND DISSOCIATION ENERGIES

For reactions (2, -2) we may write

$$\Delta H_2^{\ominus} = E_2 - E_{-2} = D(i - C_3 F_7 - H) - D(H - Br).$$
⁽²¹⁾

 E_{-2} was not measured, but from eqn (8) we have

$$E_{-2} - E_3 = 10.9 \pm 0.7 \text{ kJ mol}^{-1}$$
.

 E_3 is unknown, but Whittle and coworkers^{10, 11} obtained $E_{22} = 2.9 \pm 2.0$ kJ mol⁻¹ for the analogous reaction

$$CF_3 + Br_2 \rightarrow CF_3Br + Br.$$
 (22)

We shall assume that E_3 has the same value, hence $E_{-2} = 13.8 \pm 2.1$ kJ mol⁻¹. Using $E_2 = 82.0 \pm 1.2$ kJ mol⁻¹ recommended above, we have $\Delta H_2^{\ominus} = 68.2 \pm 2.4$ kJ mol⁻¹ at a mean temperature of 293 °C. Heat capacities are not available for reaction (2) so we assumed that $\Delta C_p(2)$ is the same as that for the corresponding reaction involving CF₃H. Using C_p data from ref. (7), $\Delta H_2^{\ominus} = 67.0 \pm 2.4$ kJ mol⁻¹ at 298 K. Introducing D(H-Br) = 366.3 kJ mol⁻¹ [ref. (7)] into eqn (21) leads to

$$D(i-C_3F_7-H) = 433.3 \pm 2.4 \text{ kJ mol}^{-1}$$
 at 298 K.

We can calculate $D(i-C_3F_7-Br)$ in a similar way using

$$\Delta H_{-3}^{\Theta} = E_{-3} - E_3 = D(i - C_3 F_7 - Br) - D(Br - Br).$$
(23)

From eqn (9), $E_{-3} = 86.3 \pm 4.2$ and we used $E_3 = 2.9 \pm 2.0$ above, hence $\Delta H_{-3}^{\ominus} = 83.4 \pm 4.7$ kJ mol⁻¹ at a mean temperature of 346 °C. Correction to 298 K, as above, leads to $\Delta H_{-3}^{\ominus} = 80.9 \pm 4.7$. Using data from ref. (7), D(Br-Br) = 192.9 kJ mol⁻¹, hence

$$D(i-C_3F_7-Br) = 273.8 \pm 4.7 \text{ kJ mol}^{-1}$$
 at 298 K.

We next consider $D[(CF_3)_3C-H]$. In section 5 we obtained an approximate value of 23 kJ mol⁻¹ for the difference $E_{18} - E_{19}$ for the activation energies for attack of Cl atoms on $(CF_3)_3CH$ and $i-C_3F_7H$, respectively. If we assume that the reverse of reactions (18) and (19) have the same activation energy then

$$\Delta H_{18}^{\ominus} - \Delta H_{19}^{\ominus} = (E_{18} - E_{-18}) - (E_{19} - E_{-19}) = E_{18} - E_{19} = 23 \text{ kJ mol}^{-1}$$

but $\Delta H_{18}^{\ominus} - \Delta H_{19}^{\ominus} = D[(CF_3)_3C - H] - D(i-C_3F_7 - H)$. Using $D(i-C_3F_7 - H)$ given above, we have $D[(CF_3)_3C - H] \approx 456$ kJ mol⁻¹. This bond dissociation energy is approximate in view of the assumptions involved in its derivation. It can be used to estimate E_{17} , the activation energy of abstraction of H from $(CF_3)_3CH$ by Br. For reaction (17)

$$\Delta H_{17}^{\ominus} = D[(CF_3)_3C-H] - D(H-Br) = E_{17} - E_{-17}$$

Taking⁷ $D(H-Br) = 369 \text{ kJ mol}^{-1}$ at 240 °C and assuming that $E_{-17} = 14 \text{ kJ mol}^{-1}$, as for i-C₃F₇+HBr, (see section 2), we have $E_{17} = 101 \text{ kJ mol}^{-1}$. This is the origin of the result given in table 3.

In table 4 we compare the above bond dissociation energy with other related values. The values quoted need some comment. The D(C-H) for the alkane series are taken from a review by McMillen and Golden.¹² However, there is evidence¹³⁻¹⁵ that some of their values other than $D(CH_3-H)$ may be slightly low. If these D(R-H) were raised, this would lead to corresponding increases in D(R-Br) for alkyl bromides. The values of D(R-H) and D(R-Br) for the perfluoroalkyl series are based on much inter-linked kinetic and equilibrium data including links to $D(CH_3-H)$. McMillen and Golden recommended a higher value of $D(CH_3-H)$ than has been used until recently. If accepted, this suggests that the results in columns 2 and 4 of table 4 may need reassessment. However, this is not practicable here in view of the complexity of

R	D(R—H)	ref.	D(R-Br)	ref.
CF ₃	445	1	291	d
C,F,	429	2	288	е
n-C ₃ F ₂	432	с	279	f
i-C ₃ F ₇	433	b	274	Ď
(CF _a) _a C	456	b	·	_
ČH,	440	g	297	g
C,H,	41 1	g	284	g
n-C ₃ H,	410	g	286	g
i-C ₃ H,	398	g	286	g
(CH ₃) ₃ C	390	g	282	g

Table 4. Some bond dissociation energies^a</sup>

^a kJ mol⁻¹. ^b Present work. ^c For the reactions $Br+n-C_3F_7H \rightleftharpoons HBr+n-C_3F_7$, *E* (forward) = 79.8 from ref. (1). Assume *E* (back) is same as for $i-C_3F_7+HBr$, *i.e.* 13.8 (see discussion, present work). Hence, using analogue of eqn (21), $D(n-C_3F_7-H) = 432$ kJ mol⁻¹. ^d Derived from $D(CF_3-H)$ in column 1 and $D(CF_3-H)-D(CF_3-Br)$ from equilibrium work.¹⁹ ^e Mean of two results: first from $D(C_2F_5-H)$ from column 1 and $D(C_2F_5-H) = 288$ kJ mol⁻¹. Second value is $D(C_2F_5-Br) = 287$ kJ mol⁻¹ from ref. (21). ^f Derived as in (d) but using data from ref. (19). ^g D(R-H) from ref. (12). D(R-Br) based on $\Delta H_f^{\ominus}(R)$ from ref. (12) and $\Delta H_f^{\ominus}(RH)$ from ref. (22). Note that D(R-H) other than $D(CH_3-H)$ may be a little low – see discussion of present work.

BROMINATION OF FLUOROALKANES

the links between the data. Any changes would be to higher values but would probably be small since several of the determinations are independent of $D(CH_3-H)$.

The progressive decrease in D(C-H) from CH_3 —H to t-Bu—H is well known and is usually explained in terms of increased stability of the radical caused by increased opportunities for hyperconjugation. Our new results for the perfluoroalkyl series show that this effect is completely absent when CH_3 groups are replaced by electronwithdrawing CF_3 groups. Indeed, $D[(CF_3)_3C-H]$ appears to be greater than $D(CF_3-H)$ by *ca.* 11 kJ mol⁻¹.

Our result for $D[(CF_3)_3C-H]$ is admittedly approximate, but if the value is correct this is probably the strongest known C-H bond in a saturated organic compound. The values of D(R-H) for the perfluoroalkyl series have implications for the reactivities of the R radicals involved. In abstraction reactions of the type

$$R + SH \to RH + S \tag{24}$$

a trend in E_{24} usually, although not invariably, parallels a trend in ΔH_{24}^{\ominus} . This suggests that $(CF_3)_3C$ will probably be the most reactive of the fluoroalkyl radicals. The i- C_3F_7 radical should also be reactive, and unpublished work in our laboratory¹⁶ suggests that its reactivity is about the same as that of CF_3 .

It has long been known that D(C-Br) for the alkyl bromide series shows much less variation than does D(C-H) for the corresponding alkanes. There could well be even less variation if the $\Delta H_f^{\ominus}(\mathbf{R})$ in ref. (12) are too low. Thus if we use $\Delta H_f^{\ominus}(t-Bu)$ recently recommended by Canosa and Marshall¹⁴ we obtain D(t-Bu-Br) =289 kJ mol⁻¹. Our new data on $D(\mathbf{R}-\mathbf{Br})$ for perfluoroalkyl bromides show that from CF₃ to i-C₃F₇, both D(C-H) and D(C-Br) follow a similar trend. No value of $D[(CF_3)_3C-Br]$ is available.

We are currently attempting to obtain more information on bond dissociation energies of the type $D[(CF_3)_3C-X]$.

We thank Drs Golden and McMillen for communicating results prior to publication. We also thank the S.E.R.C. for grants to B.S.E. and I.W.

- ¹ J. C. Amphlett and E. Whittle, Trans. Faraday Soc., 1968, 64, 2130.
- ² B. S. Evans and E. Whittle, Int. J. Chem. Kinet., 1981, 13, 59.
- ³ P. Corbett, A. M. Tarr and E. Whittle, Trans. Faraday Soc., 1963, 59, 1609.
- ⁴ A. M. Tarr, J. W. Coomber and E. Whittle, Trans. Faraday Soc., 1965, 61, 1182.
- ⁵ J. W. Coomber and E. Whittle, Trans. Faraday Soc., 1966, 62, 1553.
- ⁶ I. Weeks and E. Whittle, to be published.
- ⁷ JANAF Thermochemical Tables (NSRDS-NBS 37) (National Bureau of Standards, Washington D.C., 1971).
- ⁸ I. Weeks, Ph.D. Thesis (University College, Cardiff, 1980).
- ⁹ S. T. Kocharyan, E. M. Rokhlin and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1967, 1847.
- ¹⁰ B. G. Tucker and E. Whittle, Trans. Faraday Soc., 1965, 61, 866.
- ¹¹ J. C. Amphlett and E. Whittle, Trans. Faraday Soc., 1966, 62, 1662.
- ¹² D. F. McMillen and D. M. Golden, Annu. Rev. Phys. Chem., 1982, in press.
- ¹³ W. Tsang, Int. J. Chem. Kinet., 1978, 10, 821.
- ¹⁴ C. E. Canosa and R. M. Marshall, Int. J. Chem. Kinet., 1981, 13, 303.
- ¹⁵ A. L. Castelhano, P. R. Marriott and D. Griller, J. Am. Chem. Soc., 1981, 103, 4263.
- ¹⁶ C. Stock, Ph.D. Thesis (University College, Cardiff, 1978).
- ¹⁷ P. C. Anson, P. S. Fredricks and J. M. Tedder, J. Chem. Soc., 1959, 918.
- ¹⁸ G. C. Fettis, J. H. Knox and A. F. Trotman-Dickenson, J. Chem. Soc., 1960, 4177.
- ¹⁹ J. W. Coomber and E. Whittle, Trans. Faraday Soc., 1967, 63, 608.
- ²⁰ G. S. Buckley, W. G. F. Ford and A. S. Rodgers, Thermochim. Acta, 1981, 49, 199.
- ²¹ K. C. Ferguson and E. Whittle, J. Chem. Soc., Farday Trans. 1, 1972, 68, 306; 641.
- ²² J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic Press, London, 1970).