

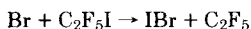
The Kinetics of the Reactions of C_2F_5 Radicals with Br_2 and HBr

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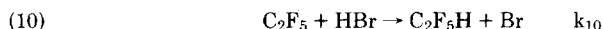
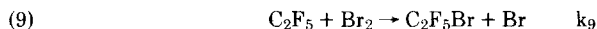
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Abstract

A mixture of $Br_2 + HBr + C_2F_5I$ was photolyzed in the vapor phase. The reaction



forms C_2F_5 radicals which are removed by



Competitive studies over the range of 74–146°C gave ratios of k_{10}/k_9 , and these were combined with values obtained previously by different methods at higher temperatures up to 515°C to give

$$\log(k_{10}/k_9) = (-0.47 \pm 0.03) - (12,500 \pm 300)/\theta$$

where $\theta = 2.303RT$ J/mol. A value is assigned to the activation energy E_{10} , and this, with other data, leads to

$$D(C_2F_5 - H) = 429.8 \pm 2.1 \text{ kJ/mol}$$

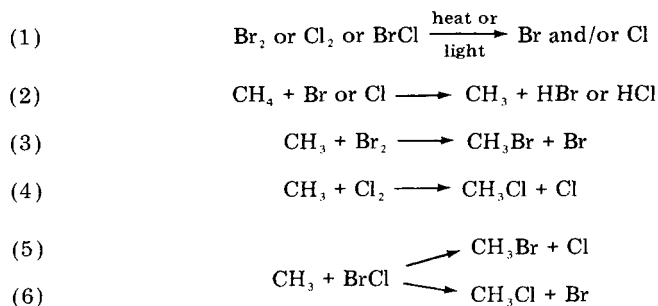
at 25°C. This result is in excellent agreement with two previous independent determinations.

Introduction

We have described previously [1] a general method which gives information about the Arrhenius parameters of the reactions between radicals and halogens. The method involves the reaction between a substrate RH and a mixture of halogens which may include interhalogen compounds. One or more of the halogens is decomposed to atoms by means of heat or light, and the atoms abstract H from RH, producing the radical of interest R which then reacts with the halogens present. This indirect production of R avoids problems associated with direct production of R by photolysis or thermolysis of the usual sources (see [1]). We first studied the system

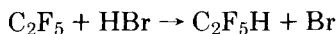
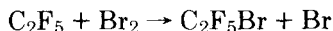
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$\text{CH}_4 + \text{Br}_2 + \text{Cl}_2$ where the reactions of interest are



That work gave relative Arrhenius parameters for reactions (3)–(6).

We now describe a variation of the method involving the competitive reactions of the C_2F_5 radical with Br_2 and HBr . The radical source is not RH but an iodide, and the reactions of interest are



The activation energies of the last two reactions are important in kinetic determinations of the bond dissociation energies $D(\text{C}_2\text{F}_5 - \text{H})$ and $D(\text{C}_2\text{F}_5 - \text{Br})$.

Experimental

Materials

A.R. Br_2 and HBr were as before [2, 3]. $\text{C}_2\text{F}_5\text{I}$ was from Fluorochem. $\text{C}_2\text{F}_5\text{Br}$ was made by mixing the vapor of $\text{C}_2\text{F}_5\text{I}$ with excess Br_2 and leaving for 10 hr at 200°C . The equilibrium lies completely on the $\text{C}_2\text{F}_5\text{Br}$ side. The products were passed several times over KOH pellets and finally through a column of auramine on brick dust. This removed all halogens and left only $\text{C}_2\text{F}_5\text{Br}$. $\text{C}_2\text{F}_5\text{H}$ was prepared by the method of Lazerte and co-workers [4]. All materials were given bulb-to-bulb distillations with middle cuts being retained. No impurities could be detected in the $\text{C}_2\text{F}_5\text{X}$ compounds by gas-liquid chromatography (GLC) or infrared spectroscopy.

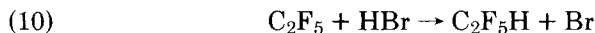
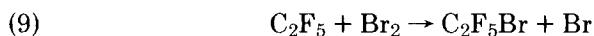
Apparatus and Procedure

This was essentially as before [1]. Reactants were mixed in the order Br_2 , $\text{C}_2\text{F}_5\text{I}$, HBr . The mixtures were photolyzed in the range of 74 – 146°C using a parallel beam of light from an ME/D 250-W mercury lamp (Osram)

filtered through a cobalt glass to remove ultraviolet light. For each run a sample of reaction mixture S_0 was withdrawn *before* photolysis, and it was analyzed by GLC at room temperature using a column of Poropak Q (length 13 cm) preceded by a scrubber column of 25% auramine on brick dust (length 25 cm) to remove halogens. During each photolysis at least three samples S_1 , S_2 , and S_3 were removed after various photolysis times, and each was analyzed by GLC. Typical photolysis times for the three samples were 30, 60, and 90 min at 74°C and 20, 40, and 60 sec at 146°C. The absolute ratio of the products (C₂F₅H)/(C₂F₅Br) was determined using a calibration mixture of C₂F₅H + C₂F₅Br as a reference.

Results and Discussion

The blue light used for photolysis was absorbed only by the Br₂. The expected reactions are



Reaction (8) is so fast [5] that it will remove most Br produced by reaction (7). If reactions (9) and (10) are the only sources of C₂F₅Br and C₂F₅H, respectively, then

$$(12) \quad \beta = \frac{R_{\text{C}_2\text{F}_5\text{H}}}{R_{\text{C}_2\text{F}_5\text{Br}}} = \frac{k_{10}(\text{C}_2\text{F}_5)(\text{HBr})}{k_9(\text{C}_2\text{F}_5)(\text{Br}_2)} = \frac{k_{10}(\text{HBr})}{k_9(\text{Br}_2)}$$

Equation (12) should be applicable, irrespective of how the Br atoms are formed, i.e., it is immaterial whether Br is formed by reaction (7) or by homogeneous or heterogeneous pyrolysis of Br₂ (or by any other process that yields Br).

To test eq. (12), we photolyzed mixtures of C₂F₅I + Br₂ + HBr in the range of 74–146°C. Reaction mixtures were left in the dark for up to 100 min before a prephotolysis sample S_0 was removed and analyzed by GLC. In no case did S_0 contain C₂F₅Br or C₂F₅H, hence there is no dark reaction.

Equation (12) requires that the ratio of products, denoted by β , be independent of photolysis time. In practice this does not happen since Br₂ and HBr are consumed at different rates, so the ratio (Br₂)/(HBr) changes as the photolysis proceeds. Hence for each run at least three samples were removed from the reaction vessel after successive intervals of photolysis, and the value of β was determined for each sample. A plot of β against photolysis time gave the true value β_0 at zero time.

TABLE I. Photolysis of mixtures of $\text{Br}_2 + \text{HBr} + \text{C}_2\text{F}_5\text{I}$.

Initial press/Torr		(HBr)	$\left\{ \frac{(\text{C}_2\text{F}_5\text{H})}{(\text{C}_2\text{F}_5\text{Br})} \right\}_{t=0}$	$k_{10} \times 10^3$
Br_2	HBr	(Br_2)		k_9
<u>T = 74°C</u>				
9.7	145	14.9	0.056	3.8
4.9	104	21.2	0.082	3.9
3.2	124	39	0.137	3.5
2.5	148	60	0.246	4.1
2.2	175	80	0.369	4.6
1.9	188	98	0.381	<u>3.9</u>
mean				<u>4.0</u>
<u>T = 120.5°C</u>				
9.9	103	10.4	0.080	7.7
5.1	103	20.2	0.130	6.4
3.9	99	25.5	0.188	7.4
3.0	159	54	0.474	8.8
2.1	142	68	0.604	8.9
1.8	148	82	0.680	8.3
1.6	149	96	0.887	<u>9.2</u>
weighted mean				<u>8.4</u>
<u>T = 146°C</u>				
12.1	131	10.8	0.087	8.1
7.1	147	20.8	0.160	7.7
4.9	193	40	0.350	8.8*
3.8	159	43	0.400	9.3
3.1	196	63	0.580	9.2
2.5	194	77	0.700	9.1
2.5	212	87	0.830	<u>9.5</u>
weighted mean				<u>9.0</u>

$\text{C}_2\text{F}_5\text{I}$ pressure normally ~ 70 torr but 35 torr in run marked with asterisk.

A series of runs were done at each of the temperatures of 74, 120.5, and 146°C, and the results are given in Table I. If eq. (12) is valid at any given temperature, a plot of β_0 against the ratio $(\text{HBr})/(\text{Br}_2)$ should be a straight line passing through the origin. Such plots, shown in Figure 1, confirm that eq. (12) applies to our results within experimental error. The value of β_0 should be independent of the initial pressure of $\text{C}_2\text{F}_5\text{I}$. A run at 146°C with half the usual pressure of $\text{C}_2\text{F}_5\text{I}$ gave an unchanged value of β_0 (see Table I).

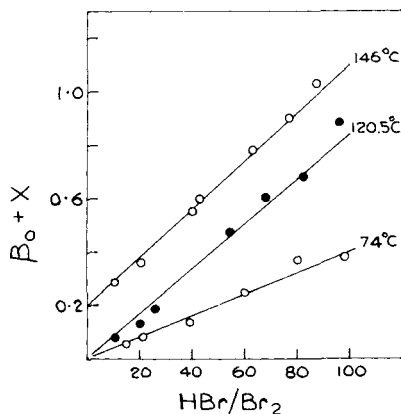


Figure 1. Plot of $X + \beta_0 = X + \{R_{C_2F_5H}/R_{C_2F_5Br}\}_0$ vs. $(HBr)/(Br_2)$. At 74 and 120.5°C, $X = 0$, at 146°C, $X = 0.2$.

It follows from eq. (12) that the slope of each line in Figure 1 gives k_{10}/k_9 at each temperature. A least-squares treatment of the data at each temperature gives lines that do not pass exactly through the origin, although the discrepancy is well within experimental error. We consider that Figure 1 confirms the validity of eq. (12) within experimental error, so we have used the equation to calculate k_{10}/k_9 for each run in Table I, with a mean k_{10}/k_9 being quoted at 74°C. At 120.5 and 146°C weighted mean values of k_{10}/k_9 are given, since we believe that k_{10}/k_9 ratios based on the higher values of β_0 are slightly more accurate.

An Arrhenius plot of k_{10}/k_9 will give the ratio of preexponential factors A_{10}/A_9 and the activation energy difference $E_{10} - E_9$. However, the ratio k_{10}/k_9 is insensitive to temperature change, so an Arrhenius plot based only on our present data would not lead to accurate results. Fortunately our present "low-temperature" results complement previous "high-temperature" results. The thermal bromination of C₂F₅H was studied by Amphlett and Whittle [6] in the range of 370–458°C. Their experiments on the inhibition of the bromination by added HBr gave values of k_{10}/k_9 over the temperature range used. Ferguson and Whittle [7] studied the kinetics of the reaction between HBr and C₂F₅Br and obtained k_{10}/k_9 over the range of 365–515°C. The values of k_{10}/k_9 from [6, 7] are given in Table II, which also includes our present mean values from Table I. It should be noted that k_{10}/k_9 at any given temperature in Table II is derived from several kinetic runs. An Arrhenius plot using all the data in Table II is shown in Figure 2. It is seen that the three sets of data fit a common line. A least-square analysis was done using a weighting for each point dependent on the number of runs on which it is based (e.g., in Table II, the result at 74°C was entered six times). The least-square analysis yielded

$$(13) \quad \log(k_{10}/k_9) = (-0.47 \pm 0.03) - (12,500 \pm 300)/\theta$$

TABLE II. Values of the ratio k_{10}/k_9 at different temperatures.

Temp./°C	$3 + \log k_{10}/k_9$	Number of runs at each temp.	Ref.
74	0.60	6	} a
120.5	0.92	7	
146	0.95	7	
370	1.62	3	} [6]
403	1.68	4	
427	1.72	2	
458	1.72	5	
365	1.48	3	} [7]
395	1.50	7	
447	1.59	5	
481	1.60	6	
515	1.55	3	

^a Present work.

where $\theta = 2.303RT$ J/mol. Error limits are standard deviations. Equation (13) gives our best current estimates of A_{10}/A_9 and $E_{10} - E_9$ and supersedes results in [6] and [7].

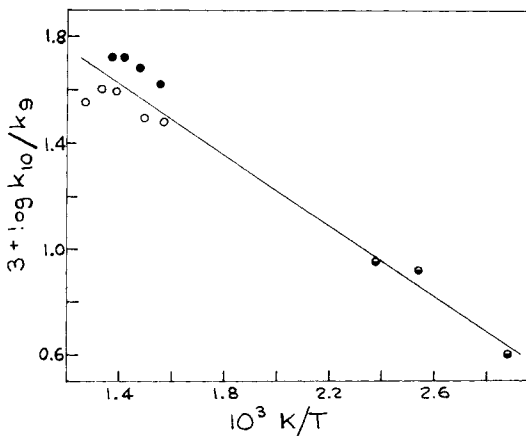


Figure 2. Arrhenius plot for k_{10}/k_9 . Data from Table II. (●) present work; (○) ref. [6]; (○) ref. [7].

An inspection of Table II and Figure 2 shows that the differences between the data from [6] and from [7] are greater than random error, which suggests that there is a small systematic discrepancy between the results from the two studies. It is therefore possible that we should combine our present results exclusively with those from [6] or from [7]. Least-square analyses then lead to $E_{10} - E_9 = 14.3 \pm 0.2$ using our present results plus data from [6], whereas using present results plus [7], we obtain $E_{10} - E_9 = 11.7 \pm 0.2$ kJ/mol. The error limits are the same in both cases, which suggests that our equal weighting of all data in Table II is probably the most reasonable way to handle the combined results.

The above discussion indicates that reaction (8) is a convenient way of making C₂F₅ radicals from C₂F₅I in the presence of halogens and hydrogen halides. The method could easily be extended to production of other fluoroalkyl radicals from fluoroiodides such as those studied by Okafo and Whittle [5].

The indirect generation of R radicals by

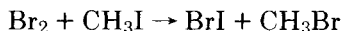


involves a class of reactions with substantially lower activation energies than the corresponding



If bromine atoms are formed by thermal decomposition of Br₂, reactions (15) and (16) can be used as sources of R radicals in the approximate range of 350–500°C, whereas if Br is generated photolytically from Br₂, reaction (14) can be used to produce R almost down to room temperature. Hence it is possible to study the reactions of any fluoroalkyl radical with, say, Br₂ + HBr over the exceptionally wide temperature range of about 450°C.

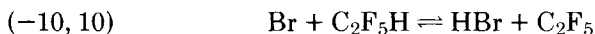
In principle the generation of radicals from iodides by reactions such as (8) could be used to study the reactions of nonfluorocarbon alkyl radicals with halogens and hydrogen halides. However, there are possible complications which could make the system unusable. Okafo and Whittle [8] showed that the reaction



occurs rapidly *in the dark* at room temperature, whereas Br₂ + CF₃I do not react under the same conditions. The mechanism of the dark reaction is not known, but it may not involve production of CH₃ radicals, in which case the analogs of reactions (9) and (10) involving CH₃ could not be studied using the reaction Br + CH₃I → BrI + CH₃ to generate CH₃ radicals.

Determination of the Bond Dissociation Energy $D(C_2F_5 - H)$

The determination of $D(C_2F_5 - H)$ by the bromination method requires a knowledge of the activation energies of the reactions



Amphlett and Whittle [6] studied the bromination of C_2F_5H and obtained $E_{-10} = 80.8 \pm 0.3$ kJ/mol. Their results from the inhibition of the bromination by HBr together with results of Ferguson and Whittle [7] obtained from a different system gave $E_{10} - E_9 = 10.0 \pm 2.1$ kJ/mol. The value of E_9 has not been measured, so Amphlett and Whittle assumed that it is the same as E for



for which they obtained $E_{17} = 2.9 \pm 2.0$ kJ/mol [9]. Using this value, together with our new $E_{10} - E_9$ from eq. (13), we obtain $E_{10} = 15.4 \pm 2.1$ kJ/mol.

For eq. (-10, 10) we may therefore write

$$\begin{aligned} \Delta H_{(-10, 10)}^\circ &= E_{-10} - E_{10} = 80.8 - 15.4 = 65.4 \pm 2.1 \text{ kJ/mol} \\ &= D(C_2F_5 - H) - D(H - Br) \end{aligned}$$

The mean temperature of these experiments was 568K and, after correction to 298 K, we have

$$\Delta H_{(-10, 10)}^\circ = 64.1 \pm 2.1 \text{ kJ/mol}$$

At 298 K, $D(H - Br) = 365.7$ kJ/mol, hence

$$D(C_2F_5 - H) = 429.8 \pm 2.1 \text{ kJ/mol}$$

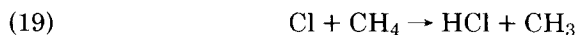
Error limits are accumulated standard deviations. This result supersedes $D(C_2F_5 - H) = 432.6$ kJ/mol, recommended by Ferguson and Whittle [7].

The above value is virtually identical to that originally recommended in [6], but the error limits are reduced. This is because the present work has yielded a more accurate value of $E_{10} - E_9$ owing to the use of a greatly extended temperature range. The biggest single source of uncertainty in the determination of $D(C_2F_5 - H)$ from bromination work is in our estimate of E_9 .

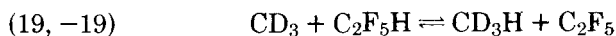
An independent determination of $D(C_2F_5 - H)$ was made by Bassett and Whittle [10] who measured the activation energy for reaction (18):



This was combined with a value of E_{-18} to give ΔH_{18}^0 and hence $D(C_2F_5 - H)$. The value of E_{-18} came from competitive work of Coomber and Whittle [11] on reaction (-18) and



This work gave $E_{19} - E_{-18}$. Bassett and Whittle used the then best current value of E_{19} to obtain $E_{-18} = 15.1$ kJ/mol. However, recent work on reaction (19), summarized by Benson and co-workers [12], indicates that, in the temperature range of 350–450 K, a better value is $E_{-18} = 12.7 \pm 0.5$ kJ/mol. This changes the value of $D(\text{C}_2\text{F}_5 - \text{H})$ obtained by Bassett and Whittle to $D(\text{C}_2\text{F}_5 - \text{H}) = 429.2 \pm 6.3$ kJ/mol. These last authors also quote a further value of $D(\text{C}_2\text{F}_5 - \text{H}) = 429.3 \pm 4.6$ kJ/mol based on activation energies for the reactions



We therefore have the following independent determinations:

$$\begin{aligned} D(\text{C}_2\text{F}_5 - \text{H}) &= 429.8 \pm 2.1 \text{ (from bromination work)} \\ &= 429.2 \pm 6.3 \text{ (from chlorination work)} \\ &= 429.3 \pm 4.6 \text{ [from reactions (19) and (-19)]} \end{aligned}$$

all at 25°C. The agreement is excellent and the value

$$D(\text{C}_2\text{F}_5 - \text{H}) = 429.4 \text{ kJ/mol}$$

should be reliable to better than ± 4 kJ/mol.

Acknowledgment

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