The Kinetics of the Gas-phase Thermal Decomposition of Bromodifluoromethane

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The pyrolysis of bromodifluoromethane has been examined over the temperature range 437—515 °C with initial pressures of reactant between 20 and 250 Torr.   The predominant mode of decomposition involves an α-elimination of hydrogen bromide to give difluoromethylene as the initial step (i) but there is also a free-radical chain component

$$CF_2HBr = CF_2 + HBr \qquad \qquad (i)$$

to the decomposition which is reduced to negligible importance by the presence of propene.   The α-elimination component of the reaction is homogeneous and of the first order in the initial stages, but inhibition by hydrogen bromide becomes important as the reaction proceeds.   The first-order rate constant obtained from the initial rates is independent of pressure and is given by log $k_1/\text{s}^{-1} = 14\cdot33 \pm 0\cdot32 - (55{,}600 \pm 1100)/4\cdot576T$.   The rate constant ($k_2$) for the reverse reaction has also been evaluated as log $k_2/\text{l mol}^{-1}\text{ s}^{-1} = 8\cdot33 \pm 0\cdot37 - (9600 \pm 1300)/4\cdot576T$ and combination of these Arrhenius parameters with the relevant heats of formation and standard entropies give $\Delta H^\circ_f(CF_2) = -42$ kcal mol^{-1} and $S^\circ(CF_2) = 66\cdot2$ cal mol^{-1} K^{-1} at 750 K, which are in good agreement with literature values.

IT is established [1-3] that the first step in the pyrolysis of chlorodifluoromethane involves the α-elimination of a molecule of hydrogen chloride to give difluoromethylene. The corresponding α-eliminations also occur in the pyrolysis of chloroform [4] and fluoroform,[5] while Simons

[1] J. W. Edwards and P. A. Small, *Ind. and Eng. Chem. (Fundamentals)*, 1965, **4**, 396.

[2] F. Gozzo and C. R. Patrick, *Tetrahedron*, 1966, **22**, 3329.

[3] G. R. Barnes, R. A. Cox, and R. F. Simmons, *J. Chem. Soc. (B)*, 1971, 1176.

[4] A. E. Shilov and R. D. Sabirova, *Zhur. fiz. Khim.*, 1959, **33**, 1365.

[5] E. Tschuikow-Roux and J. E. Marte, *J. Chem. Phys.*, 1965, **42**, 2049.

and Yarwood [6] have observed the characteristic u.v. absorption spectrum of difluoromethylene in the flash photolysis of bromodifluoromethane. The absorption bands persisted for several milliseconds after the flash and no product was detected from the simple dissociation of bromodifluoromethane into two radicals. This suggests that an α-elimination of hydrogen bromide can occur in this case, but there has been no kinetic study of the pyrolysis, although Downing et al.[7] have examined the products of the pyrolysis at 600 °C.

In contrast to reactions involving the β-elimination of hydrogen halides, where the nature of the transition state is well established, reactions involving an α-elimination are not well understood. In an attempt to gain a better understanding, therefore, the kinetics of the pyrolysis of bromodifluoromethane have been studied. Preliminary experiments indicated that the decomposition proceeded by two concurrent paths, one involving the α-elimination of hydrogen bromide as the initial step, while the other involved a decomposition into two radicals. The addition of small amounts of propene, however, rendered the importance of the chain component negligible, and this has enabled the α-elimination to be studied kinetically.

EXPERIMENTAL

The apparatus was reported earlier,[3] and the reaction was followed by the direct analysis of reaction mixtures in conjunction with the pressure variation in the reaction vessel. The pressure of the sample for analysis was first measured in a known volume and then passed through a U-tube cooled to −80 °C to remove products of low volatility. The hydrogen bromide produced in the decomposition was estimated by its direct absorption on firebrick impregnated with NN-dimethyl-p-toluidine, but since this reagent has a small vapour pressure at room temperature it was necessary to use a trap cooled to −80 °C to ensure that no absorbent was carried into the sample. The fluorocarbons in the reaction mixture were analysed by g.l.c., for which the detector element consisted of two closely matched thermistors and helium was used as the carrier gas. A 3 m column of dinonyl phthalate (30% w/w) on 30—60 mesh firebrick (flow-rate 60 cm³ min⁻¹, column temp. 20 °C) was used for the quantitative analysis of the products of the pyrolysis of pure bromodifluoromethane. When propene was present in the reaction mixture, however, it was more convenient to use a 1·5 m column of 100—120 mesh activated silica gel (flow-rate 40 cm³ min⁻¹, column temp. 95 °C). The pure components were used for calibration purposes, and the analysis of synthetic mixtures of similar composition to reaction mixtures showed that the reproducibility of the analytical method was within ±1·5%.

The products were initially identified by the comparison of retention times with those for known compounds on a 10 m column of Kel-F oil (30% w/w) on 60—80 mesh Celite (flow-rate 50 cm³ min⁻¹; column temp. 20 °C). Samples of the separated components were collected at the

outlet of the detector in U-tubes cooled to −196 °C, and the i.r. and mass spectra of the samples were determined to confirm the identification.

Materials.—Bromodifluoromethane was prepared by the fluorination of bromoform at 100 °C and 4 atm by use of antimony trifluoride which contained a small amount of antimony pentachloride.[8] The crude product was purified by low-temperature distillation on a Podbielniak column and the fraction of b.p. −15·5 and −15·0 °C was collected. The i.r. spectrum of this sample corresponded with that reported for bromodifluoromethane [9] except for a small absorption at 5·32 μm. Analysis by g.l.c. showed the presence of a trace impurity with a shorter retention time than bromodifluoromethane, but a comparison of chromatogram peak areas suggested that it only amounted to ca. 0·2% of the sample. In consequence, the sample was used without further purification.

Commercial propene was purified by fractional condensation and the middle fraction was retained. G.l.c. showed that this sample contained 5·5% propane, but no other impurity was detected. This small amount of propane was recovered unchanged when the propene was used as an inhibitor in the pyrolysis, and obviously did not interfere in the reaction. Hydrogen bromide (Matheson Chem. Co., quoted purity 99·8%) was 'degassed' and used without further purification. Samples of tetrafluoroethylene, difluoromethane, dibromodifluoromethane, and 1-bromo-1,1,2,2-tetrafluoroethane were available for g.l.c. calibration.

RESULTS

The pyrolysis of pure bromodifluoromethane was examined at 466 and 495 °C with initial pressures of 100—300 Torr and it was found that the products were hydrogen bromide, tetrafluoroethylene, difluoromethane, dibromodifluoromethane, 1-bromo-1,1,2,2-tetrafluoroethane, 1-bromo-1,1,2,2,3,3-hexafluoropropane, and perfluorocyclobutane. Figures 1 and 2 show some typical results for the consumption of reactant and the appearance of the major products, and to facilitate the comparison of results at different initial pressures these results are expressed in terms of mole % for each component. Figure 1 shows that the extent of the decomposition after a given time was not significantly affected by the initial pressure and that the reaction showed no induction period. However, a first-order function plot showed that a first-order rate law only held in the initial stages of the reaction, and the direction of the curvature indicated that the decomposition exhibits a pronounced self-inhibiting effect at finite conversion.

In the initial stages of the reaction, the amount of hydrogen bromide formed is effectively equal to the amount of bromodifluoromethane which has decomposed (Figure 1), but this does not hold throughout the reaction. Figure 2 shows that tetrafluoroethylene is the major fluorocarbon product in the initial stages, but that its concentration soon passed through a maximum. The removal of tetrafluoroethylene was presumably due to secondary reactions, since the appearance curves for 1-bromo-1,1,2,2-tetrafluoroethane and 1-bromo-1,1,2,2,3,3-hexafluoropropane

[6] J. P. Simons and A. J. Yarwood, *Nature*, 1961, **192**, 943.
[7] R. B. Downing, A. R. Benning, and R. C. McHarness, U.S.P. 2,387,247/1945.

[8] A. L. Henne, *J. Amer. Chem. Soc.*, 1937, **59**, 1200.
[9] A. Palm, F. L. Voelz, and A. G. Meister, *J. Chem. Phys.*, 1955, **23**, 726.

showed distinct induction periods. The concentrations of difluoromethane and dibromodifluoromethane were approximately equal and increased steadily during the reaction and, in the later stages of the reaction, the yields of these compounds were greater than that of tetrafluoroethylene. The total pressure passed through a pronounced maximum which corresponded closely to the maximum in the appearance curve for tetrafluoroethylene. In the above experiments the amounts of perfluorocyclobutane present were not determined, since this compound was not sufficiently separated from tetrafluoroethylene by the dinonyl phthalate column. Separate analyses using the Kel-F column, however, showed that these amounts were small compared with the amounts of the other fluorocarbon products.

the formation of difluoromethane was unaffected (see Table 1). This suggests that the formation of tetrafluoroethylene involves an intermediate which also reacts with propene, and it should be noted that the amounts of
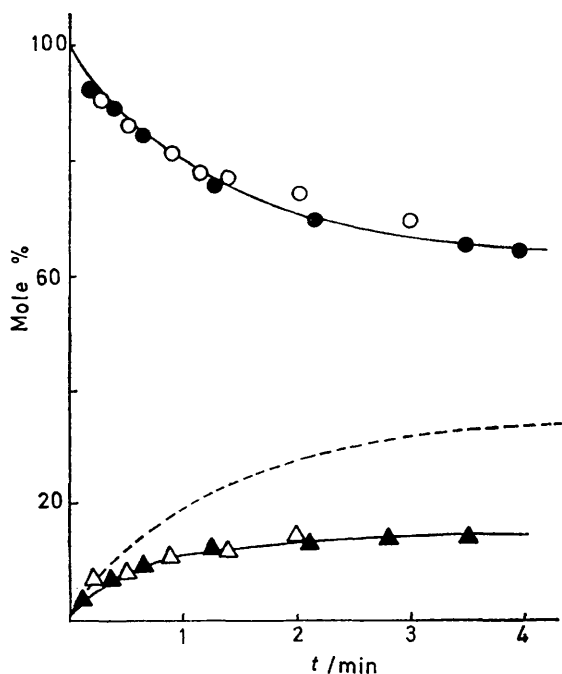

FIGURE 1 The disappearance of reactant and appearance of hydrogen bromide in the decomposition of bromodifluoromethane. Temp. 466 °C. ●, ○ CF₂HBr; ▲, △ HBr. Initial pressures: ●, ▲ 100 Torr; ○, △ 200 Torr. - - - - Expected yield of HBr from 2CF₂HBr = 2HBr + C₂F₄
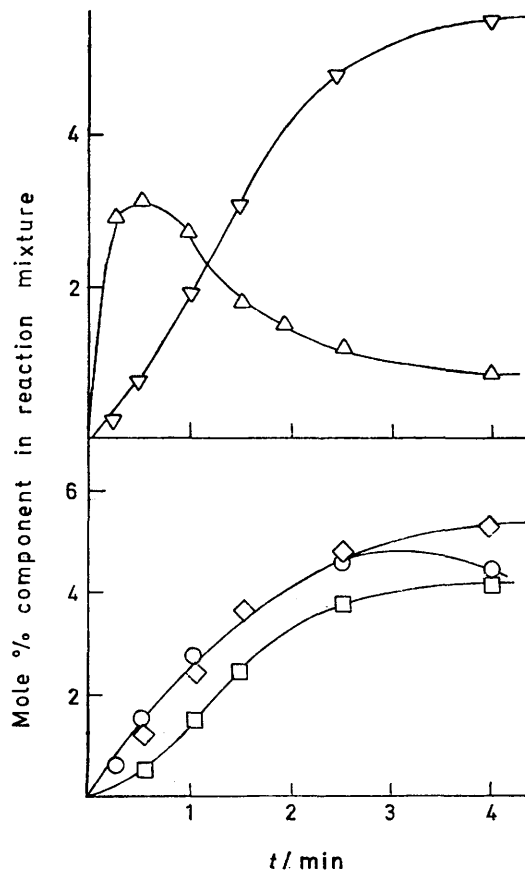

FIGURE 2 Appearance of products in the decomposition of bromodifluoromethane. Temp. 495 °C. Initial pressure 100 Torr. △ C₂F₄; ▽ C₂F₄HBr; ○ CF₂H₂; ◇ CF₂Br₂; □ C₃F₆HBr
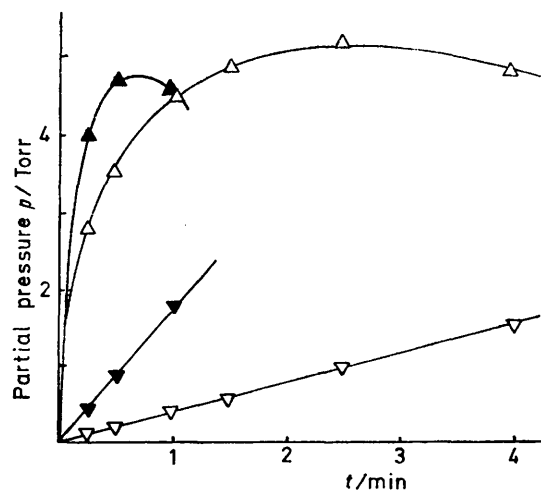
The addition of propene suppressed the formation of dibromodifluoromethane, 1-bromo-1,1,2,2-tetrafluoroethane, and 1-bromo-1,1,2,2,3,3-hexafluoropropane and Figure 3 shows that the rate of formation of difluoromethane was significantly reduced. This clearly indicates that a freeradical chain mechanism is involved in the formation of these products. In contrast, Table 1 shows that propene has no marked inhibiting effect on the rate of decomposition of reactant in the early stages, and Figure 4 shows that under these conditions the amount of hydrogen bromide formed was always very close to the amount of bromodifluoromethane decomposed. Figure 3 also shows that the initial rate of formation of tetrafluoroethylene was slightly reduced by the propene, but there was no sharp decline in its concentration as the reaction proceeded. Increasing the amount of propene present reduced the initial rate of formation of tetrafluoroethylene, whereas

FIGURE 3 The effect of added propene on the appearance of products in the decomposition of bromodifluoromethane. Temp. 483·5°. Initial pressure 100 Torr. ▲, △ C₂F₄; ▼, ▽ CF₂H₂; △, ▽ C₃H₆ present; ▲, ▼ no C₃H₆ present

'high boilers', *i.e.*, products of low volatility, increased significantly when propene was present (see Table 1). This was partially due, however, to a direct reaction between tetrafluoroethylene and propene at the reaction temperatures, which gives 1-methyl-2,2,3,3-tetrafluoro-cyclobutane (b.p. 68·3 °C). Although propene itself is stable at the temperatures used in this study, some cracking of the propene occurred since small amounts of hydrogen and methane were also formed.

The above results clearly indicate that the decomposition of pure bromodifluoromethane proceeds by two concurrent mechanisms. The first is a chain process in which difluoromethane is formed, but Table 1 shows that <1%
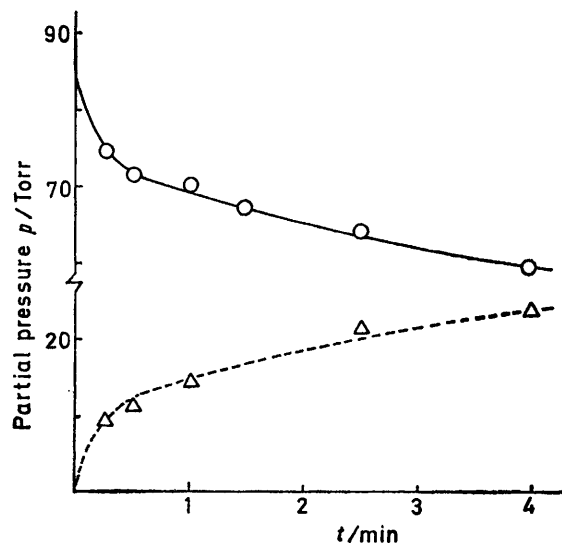

FIGURE 4 The disappearance of reactant and appearance of hydrogen bromide in the decomposition of bromodifluoromethane in the presence of propene. Initial pressures: CF_2HBr 85 Torr, C_3H_6 15 Torr. Temp. 483·5 °C. $\bigcirc$ CF_2HBr, $\triangle$ HBr. – – – – Expected yield of HBr from $2CF_2HBr = 2HBr + C_2F_4$

TABLE 1

Effect of added propene on the pyrolysis of bromodifluoromethane

Temp. 489 °C; total pressure 200 Torr

Initial pressures p/ Torr		Apparent first-order rate constants * from:			'High-boilers' formed in
CF_2HBr	C_3H_6	CF_2HBr	C_2F_4	CF_2H_2	1·5 min (mole %)
200	0	1·54	0·46	0·029	<1·0
175	25	1·60	0·46	0·0062	1·7
164	36	1·58	0·38	0·0067	1·7
150	50	1·47	0·33	0·0073	2·3
130	70	1·54	0·28	0·0074	2·5

* Expressed as $(d[\text{component}]/dt)_0$/Initial pressure of CF_2HBr.

of the bromodifluoromethane which decomposes appears as difluoromethane when propene is present. In the latter conditions, therefore, the second mode of decomposition predominates and it will be shown later that the initial step in this process involves the α-elimination of hydrogen bromide to give difluoromethylene. The kinetics of the decomposition of bromodifluoromethane in the presence of propene have been examined, in detail, therefore, over the temperature range 437—515 °C with initial pres-

sures of reactant between 20 and 250 Torr. The initial pressures of propene were in the range 5—25% of that of bromodifluoromethane; the larger amounts were required at the higher temperatures to ensure that the chain component of the decomposition could be neglected. Throughout the study a careful check was kept of the amount of difluoromethane formed, to ensure that this chain component of the reaction was unimportant.

The analytical results showed that the analytical method used in the present study was satisfactory, especially at the lower temperatures where the analytical balances were good. At the higher temperatures there was a significant discrepancy in the analytical balance towards the end of the reaction, but there was no evidence for the formation of any other major product. Under these latter conditions relatively large amounts of 'high-boilers' were obtained, but the amount detected was significantly less than the amount of propene consumed. This suggests that the discrepancy was due to an accumulation of minor products which are formed in reactions involving propene. There was no evidence that such products affected the decomposition of bromodifluoromethane and, since the kinetics of this decomposition had to be examined from the initial rates of reaction, the discrepancy was not considered serious.

For each set of experimental conditions at least six experiments were carried out, in which the reaction mixture was removed from the reaction vessel after different reaction times and the partial pressures of the reactant, products, and inhibitor were determined by analysis. Particular attention was paid to analyses at the beginning of the reaction so that the initial rates could be accurately defined. The reproducibility of these results was inferred both from the good analytical balances and the reproducible pressure change during the reaction. Again, the experiments were carried out in a random order, and in some cases on different days, but the experimental curves were always regular and the results of duplicate experiments agreed within the experimental error of the analytical method.

Initial rates were determined by drawing tangents to the disappearance curve for reactant at zero time and the values obtained are given in Table 2. Where the corresponding initial rates of formation of hydrogen bromide were determined these are also listed and in all cases the two values are close to each other. Since the extent of reaction was approximately independent of the initial pressure with propene present, it was suspected that the decomposition was of the first order, and the apparent first-order rate constants (initial rate of decomposition divided by initial pressure of reactant) are listed in Table 2. It was estimated that the error in the determination of the initial rates of decomposition was ±12·5%, whereas the standard deviation calculated for the apparent rate constants given in Table 2 is only ±4%. Thus the rate constants are independent of pressure (within experimental error) and the reactant initially decomposed by a first-order process. The initial rates of formation of difluoromethane were also determined and the apparent first-order rate constants in Table 2 show that the difluoromethane was formed in a first-order process.

The observed first-order rate constants for the decomposition of bromodifluoromethane and the formation of difluoromethane were represented in the Arrhenius form and in each case a good straight line was obtained. A

TABLE 2

Apparent first-order rate constants for the pyrolysis of bromodifluoromethane in the presence of propene

Temp. T/°C	Initial pressures p Torr		Initial rates of reaction Torr min^{-1}		First-order rate constants k/ min^{-1} from:	
	CF$_2$HBr	C$_3$H$_6$	CF$_2$HBr	HBr	CF$_2$HBr	CF$_2$H$_2$
437	95	5	8.7	9.0	0.091	—
451·5	95	5	17.8	20.0	0.188	—
	180	20	40	30	0.222	0.0009
469·5	90	10	45	54	0.500	0.0021
	180	20	103	96	0.590	0.0019
	270	30	147	150	0.545	0.0018
483·5	85	15	85	87	1.00	0.0046
	170	30	192	—	1.13	0.0047
494·5	20	5	40	—	2.00	—
	80	20	139	—	1.74	0.0088
	160	40	288	—	1.80	0.010
502·5	40	10	100	—	2.50	—
	75	25	190	—	2.53	0.0123
	225	75	521	—	2.32	0.0146
515·5	75	25	322	290	4.33	0.024
	150	50	560	440	3.73	0.022

least-squares fit to these plots gave an activation energy of $55\cdot6 \pm 1\cdot1$ kcal mol^{-1} with log A/s^{-1} = $14\cdot33 \pm 0\cdot32$ for the overall decomposition, and the corresponding parameters for the formation of difluoromethane were $62\cdot0 \pm 1\cdot8$ kcal mol^{-1} and log A s^{-1} = $13\cdot82 \pm 0\cdot51$. The latter activation energy is considerably higher than that for the overall decomposition, as expected if difluoromethane is not a product of the main decomposition.
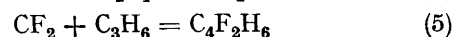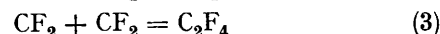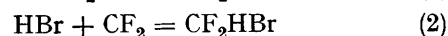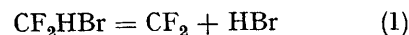
It is known that the self-inhibition observed in the pyrolysis of chlorodifluoromethane is due to the reaction of difluoromethylene with hydrogen chloride [1-3] and the corresponding reaction would also be expected to occur with hydrogen bromide. To examine whether the self-inhibition observed in the present work can be explained in this way, mixtures of reactant and propene with up to 20% added hydrogen bromide were decomposed. Both the initial rate of decomposition and the amount of tetrafluoroethylene formed markedly decreased as the initial amount of hydrogen bromide was increased, but the formation of difluoromethane was almost unaffected. It was also found that the rate of decomposition of bromodifluoromethane under given conditions was the same, whether the hydrogen bromide was formed in the decomposition or added initially.

Several experiments were carried out in a reaction vessel packed with lengths of silica tubing, which had a surface : volume ratio *ca.* 7 times greater than the unpacked vessel. These showed that the extent of decomposition and the yields of tetrafluoroethylene and difluoromethane after a given time were very similar in both the packed and unpacked vessels. In addition, the apparent first-order rate constants obtained from the initial rates at 490 °C were 1·60 and 1·62 min^{-1} respectively, which confirms that the decomposition must be homogeneous and not heterogeneous.

DISCUSSION

The results show that the reaction giving tetrafluoroethylene and hydrogen bromide is of the first order in the initial stages, essentially homogeneous, and inhibited by hydrogen bromide. The rate of this first-order reaction has also been shown to be independent of the amount of propene present and, provided there is sufficient propene, the formation of difluoromethane by a chain reaction can be neglected. The general kinetic features of the reaction are very similar to those obtained in the pyrolysis of chlorodifluoromethane so it seems likely that the present reaction occurs by the corresponding mechanism, namely reactions (1)—(5).

$$CF_2HBr = CF_2 + HBr \tag{1}$$

$$HBr + CF_2 = CF_2HBr \tag{2}$$

$$CF_2 + CF_2 = C_2F_4 \tag{3}$$

$$C_2F_4 = 2CF_2 \tag{4}$$

$$CF_2 + C_3H_6 = C_4F_2H_6 \tag{5}$$

Reaction (1) is a unimolecular α-elimination of hydrogen bromide to give difluoromethylene and direct evidence for the occurrence of reaction (2), which explains the observed inhibition by hydrogen bromide, was obtained from the pyrolysis at 495 °C of mixtures of chlorodifluoromethane and hydrogen bromide. Under these conditions the major product was bromodifluoromethane. Reaction (3) accounts for the formation of tetrafluoroethylene in the pyrolysis of chlorodifluoromethane, but reaction (4) only becomes important towards the end of the reaction. Order-of-magnitude calculations using reported values [10] for k_4 lead to the same conclusion in the present reaction. The kinetic results show that the addition of propene reduces the initial rate of formation of tetrafluoroethylene, which indicates that reaction (5) cannot be neglected. Addition reactions of difluoromethylene with various olefins to yield the corresponding cyclopropane derivatives have been reported [11] and, on this basis, the formation of 2-methyl-1,1-difluorocyclopropane might be expected, but if it is formed it probably isomerises under the present experimental conditions. No direct evidence for this reaction was obtained, as no C$_4$ fluorohydrocarbon was firmly identified in the products, although a mass-spectrometric examination of the 'high-boilers' showed that this fraction was a mixture of fluorohydrocarbons. In addition, computations showed that when reaction (5) was included in the mechanism a more realistic description of the consumption of propene was obtained than if this reaction was neglected. No perfluoropropene was detected in the products and thus the occurrence of an addition reaction between difluoromethylene and tetrafluoroethylene can be excluded.

Application of the steady-state approximation to the concentration of difluoromethylene gives a quadratic equation in [CF$_2$], and thus it is not possible to obtain a simple expression for the overall rate of reaction, but it is possible to obtain a relationship which can be tested graphically as follows. The overall rate of reaction (R) is given by equation (6) and the steady-state

[10] A. P. Modica and J. E. Lagraff, *J. Chem. Phys.*, 1965, **43**, 3383.

[11] B. Atkinson and D. McKeagan, *Chem. Comm.*, 1966, 189.

$$R = k_1[CF_2HBr] - k_2[CF_2][HBr] \qquad (6)$$

approximation leads to equation (7) and hence (8).

$$R = 2k_3[CF_2]^2 + k_5[CF_2][C_3H_6] \qquad (7)$$

$$[CF_2] = [(R - k_5[CF_2][C_3H_6])/2k_3]^{\frac{1}{2}} \qquad (8)$$

Substitution for $[CF_2]$ in equation (6) gives equation (9).

$$\frac{k_1[CF_2HBr]}{R} - 1 =$$
$$\frac{k_2[HBr]}{R^{\frac{1}{2}}}\left[\frac{1}{2k_3}\left(1 - \frac{k_5[CF_2][C_3H_6]}{R}\right)\right]^{\frac{1}{2}} \qquad (9)$$

If the rate of reaction (5) is small compared with the overall rate of disappearance of reactant, equation (9) reduces to (10). In this case, a plot of $k_1[CF_2HBr]/R$

$$\frac{k_1[CF_2HBr]}{R} - 1 = \frac{[HBr]}{R^{\frac{1}{2}}}\frac{k_2}{(2k_3)^{\frac{1}{2}}} \qquad (10)$$

against $[HBr]/R^{\frac{1}{2}}$ should give a straight line with slope $k_2/(2k_3)^{\frac{1}{2}}$ and an intercept of unity.

The reaction rate (R) was determined from tangents drawn to the concentration–time curves for bromodifluoromethane and the concentration of hydrogen bromide was taken as the amount of bromodifluoromethane which had decomposed. At higher conversions, where the inhibition by hydrogen bromide was pronounced, R was comparable in magnitude with the rate of formation of difluoromethane, and in these conditions a correction was made for the amount of bromodifluoromethane which reacted to give difluoromethane. k_1 was obtained from the initial rates of reaction, since in these conditions there is no effective contribution from reaction (2). Figure 5 gives the results plotted as required by equation (10) and it will be seen that the plots are reasonably linear with the required intercept. Further, the slope of the lines are independent of the initial pressure of reactant as required by equation (10).

The plots of equation (10) were used to determine the value of $k_2/(2k_3)^{\frac{1}{2}}$ at each reaction temperature and when the values obtained were plotted in the Arrhenius form a good straight line was obtained. A least-squares treatment of these results gave values of 8.8 ± 1.3 kcal mol^{-1} for $E_2 - E_3/2$ and $10^{4.12 \pm 0.37}$ l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ for $A_2/(2A_3)^{\frac{1}{2}}$. Dalby[12] has measured k_3 from the flash photolysis of tetrafluoroethylene and combination of his Arrhenius parameters for k_3 with those given above leads to equation (11). The error limits quoted in

$$k_2/\text{l mol}^{-1}\text{ s}^{-1} =$$
$$10^{8.33 \pm 0.37}\exp\left[-(9600 \pm 1300)/RT\right] \qquad (11)$$

equation (11) are the standard deviation of the slope and intercept from a least-squares fit of the Arrhenius plot for the values of $k_2/(2k_3)^{\frac{1}{2}}$, but they make no allowance for the uncertainty in the values of k_3 or for the assumptions involved in deriving the values of $k_2/(2k_3)^{\frac{1}{2}}$. As a result, the realistic error limits for k_2 are somewhat greater than indicated above.

Reaction (2) is the reverse of reaction (1) and thus the

Arrhenius parameters for these two reactions can be combined to obtain values for the heat of formation $[\Delta H_f^\circ(CF_2)]$ and the entropy of formation $[S^\circ(CF_2)]$ of difluoromethylene at 750 K (the average temperature of the experiments). $\Delta H_f^\circ(CF_2)$ is related to the heat of reaction (1) by the relation (12) where

$$\Delta H_f^\circ(CF_2) =$$
$$\Delta H_1^\circ + \Delta H_f^\circ(CF_2HBr) - \Delta H_f^\circ(HBr) \qquad (12)$$

$\Delta H_1^\circ = E_1 - E_2$. $\Delta H_f^\circ(HBr) = -12.7$ kcal mol^{-1} at 750 K,[13] but the heat of formation of bromodifluoromethane does not appear to have been determined
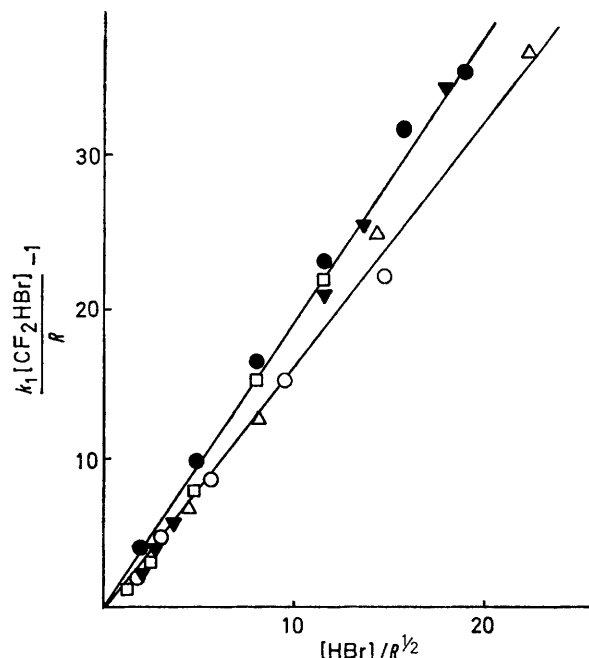

FIGURE 5   Variation of $k_1[CF_2HBr]/R$ with $[HBr]/R^{\frac{1}{2}}$. Temperatures: filled points 515.5 °C; open points 502.5 °C. Initial total pressures: □ 50 Torr; ○, ● 100 Torr, ▼ 200 Torr; △ 300 Torr

experimentally. However, Bernstein[14] has calculated the heats of formation of a number of halogenated methanes from the contributions of the individual bonds and the interactions within the molecules, and where experimental values are available the calculated results are in excellent agreement with them. These calculations give $\Delta H_f^\circ(CF_2HBr) = -98$ kcal mol^{-1} at 298 K which corresponds to a value of -101 kcal mol^{-1} at 750 K. Thus $\Delta H_f^\circ(CF_2)_{750} = -42 \pm 3$ kcal mol^{-1}, which is very close to the currently accepted value of ca. -40 kcal mol^{-1} at 298 K. The entropy change for reaction (1) (ΔS_1°) calculated from the pre-exponential factors for reactions (1) and (2) is $\Delta S_1^\circ = 33.5$ cal mol^{-1} K^{-1} (based on a standard state of 1 atm). When this is combined with values of S° at 750 K for hydrogen bromide and bromodifluoromethane of 53.8 and 86.5 cal

[12] F. W. Dalby, *J. Chem. Phys.*, 1964, **41**, 2297.
[13] JANAF Thermochemical Tables, 1961.
[14] H. J. Bernstein, *J. Phys. Chem.*, 1965, **69**, 1550.

mol^{-1} K^{-1} respectively,[13] the value obtained for $S°(CF_2)$ is $66 \cdot 2$ cal mol^{-1} K^{-1}, which should be compared with the literature value of $66 \cdot 5$ cal mol^{-1} K^{-1} at 750 K. This close agreement between the literature values for $\Delta H_f°(CF_2)$ and $S°(CF_2)$ and those obtained from the Arrhenius parameters for reactions (1) and (2) confirms that the kinetic analysis of the results is essentially correct.

Table 3 compares the Arrhenius parameters obtained for reaction (1) with those for other α-elimination re-

TABLE 3

Arrhenius parameters for some simple α-elimination reactions

Reaction	log A/s^{-1}	E/kcal mol^{-1}	Ref.
CF$_2$HCl = CF$_2$ + HCl	13·84	55·8	1
CF$_2$HBr = CF$_2$ + HBr	14·33	55·6	This work
CF$_3$H = CF$_2$ + HF	12·10	63·0	5
CCl$_3$H = CCl$_2$ + HCl	11·42	47·0	4

actions in which a molecule of hydrogen halide is eliminated. The pre-exponential factors for the decomposition of chlorodifluoromethane and bromodifluoromethane are very similar and appear to be normal for the unimolecular decomposition of small molecules. The pre-exponential factor for the decomposition of fluoroform is significantly lower, but the decomposition has only been studied in shock-tube experiments, where it was found that at 1400 K the apparent first-order rate constant was pressure-dependent up to 18 atm. Thus there may be some uncertainty in the interpretation of the results in this case and the reported Arrhenius parameter may not be very reliable. A rather low value of the pre-exponential factor has also been reported for the α-elimination of hydrogen chloride from chloroform, and in view of the similarity between the reactant molecules this is surprising.

The most probable transition state for an α-elimination reaction is a three-centre configuration. The pre-exponential factors for the decomposition of chlorodi-

fluoromethane and bromodifluoromethane, however, have values which correspond to entropies of activation of $+1 \cdot 0$ and $+3 \cdot 2$ cal mol^{-1} K^{-1} respectively. It follows that the entropy associated with the internal degrees of freedom which are lost when the transition state is formed must be regained elsewhere, and the most likely source is an increase in the rotational entropy from an elongation of the C–X bond. It is probable, therefore, that the three-centre transition state involved in these α-eliminations more closely resemble the separated entities CF$_2$ and HX than the reactant molecule, and by analogy with similar four-centre eliminations, there is probably also some polarisation of the C–X bond.

The activation energy for the formation of difluoromethane was found to be $62 \cdot 0 \pm 1 \cdot 8$ kcal mol^{-1}, and the most probable mechanism for the formation is reactions (13) and (14). Thus this activation energy may be

$$CF_2HBr = CF_2H + Br \qquad (13)$$

$$CF_2H + C_3H_6 = CF_2H_2 + C_3H_5 \qquad (14)$$
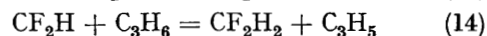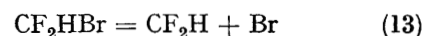
equated to $D(CF_2H–Br)$, since E_{-13} is likely to be close to zero. Sehon and Szwarc [15] have reported $D(CH_3–Br)$ = $67 \cdot 5$ kcal mol^{-1} and $D(CF_3–Br) = -64 \cdot 5$ kcal mol^{-1} and thus the above value is quite reasonable. E_{13} can also be used to estimate the heat of formation of the difluoromethyl radical, if it is assumed that $E_{-13} = 0$, and the value obtained is $\Delta H_f°(CF_2H) = 59 \cdot 3$ kcal mol^{-1}. This quantity does not appear to have been determined previously either by experiment or by calculation, but a value of this magnitude seems reasonable from a consideration of the heats of formation of the methyl and trifluoromethyl radicals ($+32 \cdot 5$ and -130 kcal mol^{-1} respectively [13]).

[15] A. A. Sehon and M. Szwarc, *Proc. Roy. Soc.*, 1951, *A*, **209**, 110.