Heat of Formation of the $CF_2Cl\cdot$ Radical

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Arrhenius parameters for the reactions:

$$CF_3\cdot + CF_2HCl \rightarrow CF_3H + CF_2Cl\cdot \quad (1)$$

$$CF_2Cl\cdot + CF_3H \rightarrow CF_2HCl + CF_3\cdot \quad (2)$$

are:

$$k_1 = 2.0 \pm 0.2 \times 10^{11} \exp(-10\,770 \pm 700/\boldsymbol{RT})\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1},$$

$$k_2 = 8.0 \pm 0.2 \times 10^{11} \exp(-13\,680 \pm 400/\boldsymbol{RT})\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

The difference in the energies of activation, combined with known thermochemical data gives a value for the heat of formation of the $CF_2Cl\cdot$ radical of −64.3 kcal and a value for $D(CF_2Cl—H)$ of 103.8 kcal. Combination of this value with the measured appearance potential of (CF_2Cl^+) from CF_2Cl_2 gives a value for the ionization potential of the $CF_2Cl\cdot$ radical of 9.1 eV. Bond-dissociation energies in several molecules containing the $CF_2Cl\cdot$ radicals have been determined from the appropriate appearance potentials of (CF_2Cl^+).

Photolysis of 1,3-dichlorotetrafluoroacetone with light of wavelength 313 nm leads to the formation of carbon monoxide and $CF_2Cl\cdot$ radicals.[1] This ketone has been used as a photochemical radical source in the study of hydrogen abstraction reactions and addition to aromatic molecules.[2] The recent determination of the heat of formation of the $CF_3\cdot$ radical by Whittle [3] and the availability of heat of formation data for CF_3H and CF_2HCl have made it possible to estimate the heat of formation of the $CF_2Cl\cdot$ radical. The hydrogen abstraction reaction from CF_2HCl by $CF_3\cdot$ radicals has been studied by the photolysis of mixtures of CF_2HCl and hexafluoroacetone at different temperatures. The reverse reaction, in which $CF_2Cl\cdot$ radicals abstract hydrogen atoms from CF_3H, has been studied by the photolysis of mixtures of CF_3H and 1,3-dichlorotetrafluoroacetone at different temperatures. In the present paper we discuss the results of these studies and combine them with known thermochemical data and with measured appearance potentials to provide estimates of the heat of formation and ionization potential of the $CF_2Cl\cdot$ radical.

EXPERIMENTAL

MATERIALS

MONOCHLORODIFLUOROMETHANE (CF_2HCl) and 1,2-DICHLOROTETRAFLUOROETHANE ($C_2F_4Cl_2$) were obtained from Imperial Chemical Industries Limited.

FLUOROFORM (CF_3H) was obtained from Cambrian Chemicals.

1,3-DICHLOROTETRAFLUOROACETONE was supplied by Koch-Light Laboratories Limited.

HEXAFLUOROACETONE was supplied by Peninsular Chemresearch Inc.

CHLOROPENTAFLUOROACETONE was supplied by Kingsley and Keith Ltd.

PROCEDURE

Sample mixtures (220 torr hexafluoroacetone and 55 torr chlorodifluoromethane or 60 torr 1,3-dichlorotetrafluoroacetone and 60 torr fluoroform) in cylindrical quartz vessels were irradiated in an aluminium block furnace at various temperatures with the light from a medium-pressure mercury vapour lamp (Phillips MBL/U 125 W) filtered as described previously [1] to isolate the 313 nm line. After irradiation the products were frozen into a U-tube cooled in liquid air and the carbon monoxide pumped to a McLeod gauge for estimation. The products were then transferred by warming to the inlet of a gas chromatography apparatus and separated upon a 0.2 in. × 5 ft column of activated alumina (for hexafluoroacetone photolysis) or a 0.2 × 6 in. column of activated alumina followed by a 0.2 in. × 15 ft column of 80/120 mesh Celite coated with 15 % w/w Kel-F no. 3 oil (for 1,3-dichlorotetrafluoroacetone photolysis). The amount of halogenated methanes and ethanes produced were determined by comparison of the gas chromatographic peak areas with those obtained from known amounts of authentic samples.

Appearance potentials of (CF_2Cl^+) were determined upon an A.E.I MS 2 mass spectrometer using methods described previously.[4]

RESULTS AND DISCUSSION

A series of photolyses was performed in which mixtures of hexafluoroacetone (220 torr) and chlorodifluoromethane (55 torr) were irradiated for 2 h at various temperatures in the range 459-517 K. The most important products of the photodecomposition are hexafluoroethane, carbon monoxide and fluoroform arising from the reactions

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

$$CF_3\cdot + CF_2HCl \rightarrow CF_3H + CF_2Cl\cdot \qquad (1)$$

$$CF_3\cdot + CF_3\cdot \rightarrow C_2F_6. \qquad (3)$$

The rates of formation of fluoroform and hexafluoroethane have been determined at a number of temperatures and the results have been plotted in the Arrhenius form against $1/T$. From the slope of the Arrhenius graph determined by a least mean squares procedure and using the literature value for k_3,[5] the Arrhenius parameters for reaction (1) have been calculated as

$$k_1 = 2.0 \pm 0.2 \times 10^{11} \exp(-10\,770 \pm 700/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}.$$

The value of the energy of activation, 10.7 kcal mol^{-1}, is of similar magnitude as that determined by previous workers [6] for hydrogen abstraction from CH_3F and CH_2F_2.

Sample mixtures of 1,3-dichlorotetrafluoroacetone (60 torr) and fluoroform (60 torr) were irradiated for 90 min at different temperatures in the range 452-509 K. The most important products of decomposition were 1,2-dichlorotetrafluoroethane, carbon monoxide and chlorodifluoromethane formed according to the reactions:

$$CF_2ClCOCF_2Cl + h\nu \rightarrow 2CF_2Cl\cdot + CO$$

$$CF_2Cl\cdot + CF_3H \rightarrow CF_2HCl + CF_3\cdot \qquad (2)$$

$$CF_2Cl\cdot + CF_2Cl\cdot \rightarrow C_2F_4Cl_2. \qquad (4)$$

The rates of formation of chlorodifluoromethane and 1,2-dichlorotetrafluoroethane have been determined and the results plotted in the Arrhenius form against $1/T$. The slope of the Arrhenius graph has been obtained by a least mean squares treatment of the results and combination of this with the measured value of the rate of recombination of this with the measured value of the rate of recombination of $CF_2Cl\cdot$ radicals, k_4,[10] gives values for the Arrhenius parameters for reaction (2) as

$$k_2 = 8.0 \pm 0.2 \times 10^{11} \exp(-13\,680 \pm 400/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}.$$

The difference between the two energies of activation is 2.9 ± 1 kcal (at an average temperature of 480 K) and this may be related to the difference in the bond-dissociation energies of fluoroform and chlorodifluoromethane, $D(CF_3—H) - D(CF_2Cl—H)$

= 2.9 kcal. A value of 106.7 kcal has been assigned to $D(CF_3—H)$ by Whittle[7] so that $D(CF_2Cl—H)$ = 103.8 kcal. This value can now be combined with values for the heat of formation of the hydrogen atom and chlorodifluoromethane to provide an estimate of the heat of formation of the $CF_2Cl\cdot$ radical:

$$D(CF_2Cl—H) = H_f(H)+H_f(CF_2Cl\cdot)-H_f(CF_2HCl).$$

$H_f(CF_2HCl)$ has been determined by Edwards and Small[8] from an equilibrium study of the pyrolysis of chlorodifluoromethane. Their value of −112.3 kcal has been corrected by reference to the presently accepted value for $H_f(HF)_{aq}$ and gives a value for $H_f(CF_2Cl\cdot)$ of -64.3 ± 2 kcal. This may be compared with the value of 69 ± 4 kcal mol^{-1} obtained by the sodium flame method.[9] Thermochemical data are not available for the heat capacities used for correcting this value to 298 K but estimates based on other halogenated methanes suggest that the correction would be at most about 0.5 kcal which is within the experimental error of the determination.

The appearance potentials of (CF_2Cl^+) from CF_2Cl_2, $C_2F_4Cl_2$, CF_3Cl, $CF_2ClCOCF_3$ and CF_2HCl have been determined. Unfortunately, the ionization efficiency curve for the last-named compound is not suitable for accurate measurements as defined previously. However, $A(CF_2Cl^+)$ = 12.55 eV from CF_2Cl may be used in the calculation of $I(CF_2Cl\cdot)$:

$$D(CF_2Cl—Cl) = H_f(Cl)+H_f(CF_2Cl\cdot)-H_f(CF_2Cl_2).$$

The presently accepted vaue for $H_f(CF_2Cl_2)$ is 115 kcal so that $D(CF_2Cl—Cl)$ = 79.6 kcal but

$$D(CF_2Cl—Cl) = A(CF_2Cl^+)-I(CF_2Cl\cdot)$$

from which $I(CF_2Cl\cdot)$ = 9.1 eV. This value lies suitably between the values of $I(CCl_3\cdot)$ = 8.5 eV and $I(CF_3\cdot)$ = 9.3 eV. Finally, this value of $I(CF_2Cl\cdot)$ may be combined with the measured values of $A(CF_2Cl^+)$ derived from various molecules to provide upper limits for the bond-dissociation energies. These results are summarized in table 1.

TABLE 1

CF_2ClX	$A(CF_2Cl^+)$ (eV)	$D(CF_2Cl—X)$ (kcal)
CF_2Cl_2	12.55	79.6
CF_3Cl	16.15	161.0
$C_2F_4Cl_2$	12.33	75.0
$CF_2ClCOCF_2Cl$	12.5	78.0

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