# Atmospheric Chemistry of CF<sub>2</sub>BrH: Kinetics and Mechanism of Reaction with F and Cl Atoms and Fate of CF<sub>2</sub>BrO Radicals

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A pulse radiolysis technique was used to investigate the kinetics and products of the reaction of CF<sub>2</sub>BrH with fluorine atoms at 296 K. This reaction forms an adduct which is in dynamic equilibrium with CF<sub>2</sub>BrH and fluorine atoms. The UV absorption spectrum of the adduct was measured relative to the UV spectrum of the CH<sub>3</sub>O<sub>2</sub> radical over the range 230–380 nm. At 280 nm, an absorption cross section of  $(1.3 \pm 0.3) \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> was determined. From the absorption at 280 nm the equilibrium constant  $K_5 = [adduct]/([F][CF_2BrH])$  was measured to be  $(1.59 \pm 0.13) \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup>. In 1 atm of SF<sub>6</sub>, the forward rate constant  $k_5 = (1.4 \pm 0.5) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and the backward rate constant  $k_{-5} = (8.8 \pm 3.0) \times 10^{5}$  s<sup>-1</sup> were determined by monitoring the rate of formation and loss of the adduct. As part of the present work a relative rate technique was used to measure  $k(Cl+CF_2BrH) = (5.8 \pm 1.0) \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 296 K and 700 Torr of N<sub>2</sub>. The fate of the oxy radical, CF<sub>2</sub>BrO, in the atmosphere is bromine atom elimination and formation of COF<sub>2</sub>.

# 1. Introduction

Halons are used as fire-extinguishing agents. The active species in halons is bromine. When heated to high temperatures, halons decompose liberating bromine atoms, which trap the free radicals that propagate combustion. However, bromine atoms are also very efficient in destroying ozone in the stratosphere.<sup>1</sup> Bromine atoms are produced by photolysis of halons in the stratosphere. CF<sub>2</sub>BrH has been proposed as a substitute for conventional fully halogenated halons. Following release into the atmosphere, hydrogen containing halogenated species react with OH radicals to produce halogenated alkyl radicals which will, in turn, react with O<sub>2</sub> to give peroxy radicals.<sup>2</sup> For example, in the case of CF<sub>2</sub>BrH:

$$CF_2BrH + OH \rightarrow CF_2Br + H_2O$$
 (1)

$$CF_2Br + O_2 + M \rightarrow CF_2BrO_2 + M$$
 (2)

In the atmosphere the peroxy radical,  $CF_2BrO_2$ , will be converted into the corresponding oxy radical,  $CF_2BrO$ . As part of a joint program between our two laboratories to survey the atmospheric fate of halogenated compounds,<sup>3-9</sup> we have conducted an experimental study of the atmospheric chemistry of  $CF_2BrH$ . A pulse radiolysis technique was used to determine absolute rate constants for individual reactions and to investigate the mechanism of the reaction of F atoms with  $CF_2BrH$ . The atmospheric fate of  $CF_2BrO$  radicals was determined using a FTIR spectrometer coupled to an atmospheric reactor. Results are reported herein.

#### 2. Experimental Section

The two different experimental systems used in the present work have been described in detail previously<sup>10,11</sup> and will only be discussed briefly here.

**2.1. Pulse Radiolysis System.** Reactions were initiated by the irradiation of  $SF_6/CF_2BrH$  and  $SF_6/CF_2BrH/CH_4$  mixtures in a 1 L stainless steel reaction cell with a 30 ns pulse of 2 MeV electrons from a Febetron 705B field emission accelerator.  $SF_6$  was always in great excess and was used to generate fluorine atoms:

$$SF_6 \xrightarrow{2 \text{ MeV } e^-} F + \text{ products}$$
 (3)

$$F + CF_2BrH \rightarrow products$$
 (4)

The radiolysis dose was varied by insertion of stainless steel attenuators between the accelerator and the chemical reactor. In this article we will refer to the radiolysis dose used in specific experiments as a fraction of the maximum dose that is achievable. The fluorine atom yield (required for quantification of UV absorption spectra) was measured by monitoring the transient absorption at 260 nm due to  $CH_3O_2$  radicals produced by radiolysis of  $SF_6/CH_4/O_2$  mixtures:

Using  $\sigma$ (CH<sub>3</sub>O<sub>2</sub>) = 3.18 × 10<sup>-18</sup> cm<sup>2</sup> molecule<sup>-1</sup>,<sup>12</sup> this absorption corresponds to a F atom yield of  $(3.2 \pm 0.3) \times 10^{15}$ molecules cm<sup>-3</sup> at full radiolysis dose and 1000 mbar of SF<sub>6</sub>.<sup>13</sup> The quoted uncertainty includes 10% uncertainty in  $\sigma$ (CH<sub>3</sub>O<sub>2</sub>) and 2 standard deviations in the absorption measurements. The uncertainties reported in this paper are 2 standard deviations unless otherwise stated. Standard error propagation methods are used to calculate combined uncertainties.

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**Figure 1.** Transient absorbance at 280 nm following the pulsed radiolysis (11% of maximum dose) of 2.5 mbar of  $CF_2BrH$  and 997.5 mbar of  $SF_6$ . The UV path length was 120 cm. The smooth line is a first-order fit to the experimental data.

Transient absorptions were followed by multipassing the output of a pulsed 150 W xenon arc lamp through the reaction cell using internal White cell optics. The physical path length of the cell is 10 cm. Total optical path lengths of 80 and 120 cm were used. After leaving the cell the light was guided through a 1 m McPherson grating UV-vis monochromator and detected with a Hamamatsu photomultiplier. All absorption transients were produced in single-pulse experiments with no signal averaging. The spectral resolution was 0.8 nm. Reagent concentrations used were as follows: SF<sub>6</sub>, 895-995 mbar; CF<sub>2</sub>BrH, 0-50 mbar; CH<sub>4</sub>, 2-40 mbar. All experiments were performed at 296 K. SF<sub>6</sub> (99.9%) was supplied by Gerling and Holz, CF<sub>2</sub>BrH (>97%) was supplied by Fluorochem Ltd., and CH<sub>4</sub> (>99%) was supplied by Gerling and Holz. All reagents were used as received. The partial pressures of the different gases were measured with a Baratron absolute membrane manometer with a detection limit of  $10^{-5}$  bar.

A Princeton Applied Research OMA-II diode array was used to measure the UV absorption spectrum of the CF<sub>2</sub>BrH–F adduct. The diode array was installed at the exit slit of the monochromator in place of the photomultiplier which was used for measuring transient absorptions. The setup consisted of the diode array, an image amplifier (type 1420-1024HQ), a controller (type 1421) and a conventional personal computer used for data acquisition, handling, and storage. Spectral calibration was achieved using a Hg pen ray lamp.

**2.2. FTIR Smog Chamber System.** The FTIR system was interfaced to a 140 L Pyrex reactor. Radicals were generated by the UV irradiation of mixtures of CF<sub>2</sub>BrH and Cl<sub>2</sub>, or F<sub>2</sub>, in 700 Torr of N<sub>2</sub>, or air diluent, at 296 K using 22 blacklamps (760 Torr = 1013 mbar). The loss of reactants and formation of products were monitored by FTIR spectroscopy, using an analyzing path length of 26 m and a resolution of 0.25 cm<sup>-1</sup>. Infrared spectra were derived from 32 coadded spectra. Reference spectra were acquired by expanding known volumes of reference materials into the reactor.

## 3. Pulse Radiolysis Results and Discussion

**3.1.** Adduct Formation from the Reaction of F with  $CF_2BrH$ . Figure 1 shows the transient absorption at 280 nm following the radiolysis (11% of maximum dose) of 2.5 mbar of  $CF_2BrH$  and 997.5 mbar  $SF_6$  using an optical path length of 120 cm. The maximum transient absorbances were measured as a function of the radiolysis dose using mixtures of 980 mbar of  $SF_6$  and either 2.5 or 20 mbar of  $CF_2BrH$ .



**Figure 2.** Maximum transient absorbance at 280 nm following the pulsed radiolysis of mixtures of 20 mbar (circles) and 2.5 mbar (squares) of  $CF_2BrH$ , respectively, and 980 and 998 mbar of  $SF_6$ , respectively, as a function of the radiolysis dose. The solid lines are linear regressions to the low dose data (filled symbols).

Figure 2 shows plots of the maximum absorbances for the two different mixtures as functions of the radiolysis dose. The maximum absorbances were linear functions of the radiolysis dose up to 50% of the full dose. The deviations from linearity at higher dose are ascribed to secondary radical-radical reactions such as self-reaction of the absorbing species or reactions between F atoms and the absorbing species. The solid lines are linear least-squares fits to the low-dose data. The slopes of the linear regressions in Figure 2 are  $2.0 \pm 0.1$  for mixtures containing 20 mbar of CF<sub>2</sub>BrH and  $0.96 \pm 0.04$  for mixtures containing 2.5 mbar of CF<sub>2</sub>BrH, respectively.

In all experiments the initial concentration of  $CF_2BrH$  is in great excess compared to that of fluorine atoms. At low doses one would expect complete conversion of F atoms to products according to reaction 4. As a consequence the absorbance

$$F + CF_2BrH \rightarrow products$$
 (4)

should be independent of the initial concentration of  $CF_2BrH$ . It is clear from Figure 2 that this is not the case and the question which arises is, "Why is the observed absorbance using an initial concentration of 2.5 mbar  $CF_2BrH$  approximately half of that observed using 20 mbar of  $CF_2BrH$ ?" The data in Figure 2 show that F atoms do not react with  $CF_2BrH$  via a simple H-atom abstraction mechanism:

$$F + CF_2BrH \rightarrow CF_2Br + HF$$
 (4a)

because, in this case the two dose plots would have the same slopes. The data in Figure 2 can be explained if the species which absorbs at 280 nm is an adduct in which a F atom is weakly bound to  $CF_2BrH$  and if the adduct is in dynamical equilibrium with F atoms and  $CF_2BrH$ :

$$F + CF_2BrH \rightleftharpoons X$$
 (5,-5)

The lower absorption observed for  $[CF_2BrH] = 2.5$  mbar compared to the absorption with  $[CF_2BrH] = 20$  mbar can be explained by a shift in the equilibrium toward the adduct at higher concentrations of  $CF_2BrH$ . In the following we shall show that all the experimental evidence can be interpreted in terms of an equilibrium between F,  $CF_2BrH$ , and the adduct X. In sections 3.2-3.6 we proceed on the assumption that reaction 4a makes a negligible contribution to the overall reaction. The validity of this assumption is discussed in section 4.2.



Figure 3. Plot of maximum absorbance as a function of  $[CF_2BrH]$ . The UV path length was 120 cm. The relative radiolysis dose was 22% of maximum dose.

**3.2. Determination of the Equilibrium Constant.** Assuming that all species behave as ideal gases the equilibrium constant of (5) is defined as

$$K_5 = k_5 / k_{-5} = [X] / ([F] [CF_2 BrH])$$

where X is the CF<sub>2</sub>BrH-F adduct.

To determine  $K_5$ , the maximum transient absorption following pulsed radiolysis of mixtures of SF<sub>6</sub> and CF<sub>2</sub>BrH at 280 nm was obtained from a double-exponential fit to the transient. The absorbance was measured at low dose (22% of maximum) where no secondary chemistry interferes with the measurements. A plot of the absorbance as a function of the initial concentration of CF<sub>2</sub>BrH is shown in Figure 3. The equilibrium constant  $K_5$ was derived from a two-parameter fit of the following expression to the experimental data:

$$A = A_r K_5 [CF_2BrH]/(1 + K_5 [CF_2BrH])$$

where *A* is the observed absorbance as a function of [CF<sub>2</sub>BrH] and  $A_x$  is the absorbance when all F atoms are converted into the adduct. The value obtained for the equilibrium constant was  $K_5 = (1.59 \pm 0.13) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ . The value obtained for  $A_x$  was  $0.48 \pm 0.01$ 

To confirm this result and to determine the rate constants for the forward and backward reactions in (5),  $k_5$  and  $k_{-5}$ , respectively, two additional sets of experiments were carried out. They are described in the following subsections.

**3.3. Determination of**  $k_5$  and  $k_{-5}$ . Another set of information can be extracted from the experiments described in section 3.2. In all experiments the initial concentration of CF<sub>2</sub>BrH is at least 35 times the concentration of F atoms and hence the loss of F atoms and the formation of products will follow pseudo-first-order kinetics. The observed transient absorbances were fit using the expression  $A(t) = (A_{inf} - A_0)[1 - \exp(-k^{1st}t)] + A_0$ , where A(t) is the time-dependent absorbance,  $A_{inf}$  is the absorbance at infinite time,  $k^{1st}$  is the pseudo-first-order formation rate of X, and  $A_0$  is the extrapolated absorbance at t = 0.

Figure 4 shows a plot of the pseudo-first-order rate constants for the formation of X,  $k^{1\text{st}}$ , as a function of the concentration of CF<sub>2</sub>BrH. The pseudo-first-order rate of formation of X increased linearly with CF<sub>2</sub>BrH concentration. Linear leastsquares analysis of the data in Figure 4 gives a slope of (1.56  $\pm$  0.31)  $\times$  10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

We assume that the formation kinetics for X are not influenced by any loss mechanism apart from decomposition



Figure 4. Plot of  $k^{1st}$  vs [CF<sub>2</sub>BrH]. See text for details.

to the parent species. This is reasonable because the decay of the adduct is much slower than its formation. At any time the concentration of F atoms will be given by  $[F] = [F]_0 - [X]$ , where  $[F]_0 = (7.0 \pm 0.7) \times 10^{14}$  molecules cm<sup>-3</sup>. The system is described as a first-order reversible reaction, and the differential equations which describe this system can be solved analytically. See, for example, ref 14, for details on the algebra. The rate law for the formation of X is

$$d[X]/dt = k'_{5}[F]_{0} - (k'_{5} + k_{-5})[X], \quad k'_{5} = k_{5}[CF_{2}BrH]$$

The solution of this nonhomogeneous first-order linear differential equation is

$$[X](t) = \frac{k'_{5}[F]_{0}}{k'_{5} + k_{-5}} (1 - \exp(-(k'_{5} + k_{-5})t))$$

The pseudo first order formation rate will be equal to  $k_5$ [CF<sub>2</sub>BrH] +  $k_{-5}$ . Hence, in Figure 4 the *y*-axis intercept gives  $k_{-5}$  and the slope gives  $k_5$ . We obtain  $k_5 = (1.56 \pm 0.31) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_{-5} = (8.3 \pm 2.5) \times 10^5$  s<sup>-1</sup>. The equilibrium constant is  $K_5 = k_5/k_{-5} = (1.8 \pm 0.8) \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup>. This is in good agreement with the value of (1.59  $\pm 0.13$ )  $\times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> obtained in section 3.2.

**3.4.** Kinetics of the CF<sub>2</sub>BrH-F Adduct in the Presence of CH<sub>4</sub>. To further confirm that the adduct X is formed in the reaction of F atoms with CF<sub>2</sub>BrH (eq 5), a set of experiments was performed with added CH<sub>4</sub> to provide a loss mechanism for F atoms (eq 6).

$$F + CH_4 \rightarrow CH_3 + HF \tag{6}$$

In these experiments the concentration of  $CF_2BrH$  was fixed at 20 mbar, the concentration of  $CH_4$  was varied over the range 2-40 mbar, and  $SF_6$  was added so the total pressure remained fixed at 1000 mbar. The transient absorption at 280 nm was observed at different concentrations of  $CH_4$ . The radiolysis dose was 22% of maximum, and the optical path length was 120 cm. Figure 5 shows the observed variation of the maximum absorbance as a function of the concentration ratio [ $CH_4$ ]/ [ $CF_2BrH$ ]. As shown in Figure 5, the addition of  $CH_4$  results in a sharp decrease in the observed absorption at 280 nm.

The CH<sub>3</sub> radical does not absorb at 280 nm and the reaction of F atoms with CH<sub>4</sub> is fast,  $k_6 = 6.8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>15</sup> CH<sub>4</sub> is an efficient scavenger of F atoms. In contrast, we do not anticipate that CH<sub>4</sub> is an efficient scavenger of other radicals potentially formed in the system. The species respon-



Figure 5. Plot of maximum absorption at 280 nm vs the concentration ratio  $[CH_4]/[CF_2BrH]$ . See text for details.

sible for the absorption at 280 nm must therefore be formed from reaction of F atoms with CF<sub>2</sub>BrH, i.e., from reaction 5.

The competition between reactions 5 and 6 was used to determine the rate constant for reaction 5. The solid line in Figure 5 represents a two-parameter fit of the following expression to the experimental data:

$$A_{\text{max}} = A_{\text{eq}} \left( 1 + \frac{k_6}{k_5} \frac{[\text{CH}_4]}{[\text{CF}_2\text{BrH}]} \right)^{-1}$$

where  $A_{\text{max}}$  is the observed maximum absorbance as a function of the concentration ratio [CH<sub>4</sub>]/[CF<sub>2</sub>BrH] and  $A_{\text{eq}}$  is the absorbance with no CH<sub>4</sub> present.  $A_{\text{eq}}$  and  $k_6/k_5$  were simultaneously varied, and the best fit was achieved with  $A_{\text{eq}} = (0.405 \pm 0.02)$  and  $k_6/k_5 = (5.42 \pm 0.81)$ . Using  $k_6 = (6.8 \pm 1.4) \times 10^{-11}$  (ref 15) gives  $k_5 = (1.25 \pm 0.25) \times 10^{-11}$  which is consistent with the value of  $k_5 = (1.56 \pm 0.31) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> determined in section 3.3. This consistency strongly suggests that the species absorbing at 280 nm is formed by the reaction of F atoms with CF<sub>2</sub>BrH. If reaction of another species with CF<sub>2</sub>BrH gave rise to the observed absorbance at 280 nm, it is highly unlikely that consistent values of  $k_5$  would be obtained from the two different techniques.

A value of  $k_{-5}$  can be obtained by observing the decay of X in the presence of CH<sub>4</sub>. The following reactions are considered:

$$F + CF_2BrH \rightleftharpoons X$$
 (5,-5)

$$F + CH_4 \rightarrow CH_3 + HF \tag{6}$$

Every time X decomposes to F atoms and  $CF_2BrH$  the F atoms can reform X via reaction 5 or be consumed by reaction 6. The fraction of F atoms reacting with methane is given by

$$f_{\rm CH_4} = \left(1 + \frac{k_5}{k_6} \frac{[\rm CF_2 Br H]}{[\rm CH_4]}\right)^{-1}$$

If all the F atoms produced from the decomposition of X are removed by reaction with methane, the decay rate of X will be  $k_{-5}$ . However, if only a fraction of F atoms is removed through this channel, the rate of decay for X is given as  $k_{decay} = f_{CH_4}k_{-5}$ . This means that if we plot  $k_{decay}$  as a function of  $f_{CH_4}$ , the slope is  $k_{-5}$ . Decay rates were obtained from experiments where the concentration of CF<sub>2</sub>BrH was held fixed at 20 mbar, the concentration of CH<sub>4</sub> was varied over the range 2–40 mbar,



Figure 6. Plot of  $k_{decay}$  vs  $f_{CH_4}$ . See text for details.

and SF<sub>6</sub> was added in an amount such that the total pressure remained fixed at 1000 mbar. The observed decay of the transient absorption was fitted using the first-order expression given in section 3.3 with t = 0 being the time for maximum absorbance and  $k^{1\text{st}}$  the decay rate of X. Figure 6 shows a plot of  $k_{\text{decay}}$  versus  $f_{\text{CH}_4}$ . The solid line is a linear regression of the experimental data which gives  $k_{-5} = (9.4 \pm 1.5) \times 10^5 \text{ s}^{-1}$ and an intercept of  $(1.3 \pm 0.9) \times 10^5 \text{ s}^{-1}$ .

The positive intercept indicates that even in the absence of methane there is a significant loss of the adduct. The intercept can be explained by radical-radical reactions such as the adduct self reaction or the existence of a loss mechanism (eq 7) for the adduct which does not involve the formation of F atoms:

$$F + CF_2BrH \rightleftharpoons X$$
 (5,-5)

$$X \rightarrow \text{products}$$
 (7)

The different values of  $K_5$ ,  $k_5$ , and  $k_{-5}$  and a short summary of how they were determined is given in Table 1. The three values calculated for  $K_5$  show good agreement.

We decide to cite a final value of  $K_5 = (1.59 \pm 0.13) \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> obtained using the method which gave the greatest precision. For  $k_5$  and  $k_{-5}$  we choose to quote values which are averages of the results in Table 1 with error limits that encompass the extremes of the ranges; hence  $k_5 = (1.4 \pm 0.5) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_{-5} = (8.8 \pm 3.0) \times 10^5$  s<sup>-1</sup>.

**3.5. Decay of the Adduct.** The decay of X was studied by radiolysis of mixtures of 20 mbar of CF2BrH and 980 mbar of  $SF_6$ . The decay of the transient absorptions were observed at 280 nm with the radiolysis dose varied over an order of magnitude. Figure 7A shows the transient absorption at 280 nm following the radiolysis at full radiolysis dose. The optical path length was 120 cm. The decay was fitted using a first order expression. Figure 8 displays a plot of  $k_{decay}$  as a function of the maximum transient absorbance. Using the steady-state approximation for X, the concentration ratio [X]/[F] is constant. In the limit of zero dose and hence zero F atoms, no secondary chemistry takes place and the only way that the concentration of X can decrease is by decomposition of X, i.e., reaction 7. The intercept in Figure 8 can therefore be interpreted as the first-order decay rate constant for reaction 7. This gives  $k_7 =$  $(7.41 \pm 0.72) \times 10^4 \text{ s}^{-1}$ .

Using the diode array the radiolysis of mixtures of 20 mbar of  $CF_2BrH$  and 980 mbar of  $SF_6$  was followed. The UV path length was 80 cm, and the resolution was 0.8 nm. Figure 9



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**TABLE 1** 

**Figure 7.** Transient absorbance following the pulsed radiolysis (A) (53% of maximum dose) of a mixture of 20 mbar of  $CF_2BrH$  and 980 mbar of  $SF_6$ . The UV path length was 120 cm. (B) Transient absorbance following the pulsed radiolysis (42% of maximum dose) at 249 nm of a mixture of 20 mbar of  $CF_2BrH$  and 980 mbar of  $SF_6$ . The UV path length was 80 cm and the resolution was 0.16 nm.



Figure 8.  $k_{decay}$  versus maximum transient absorbance. See text for details.

shows the spectrum obtained 100  $\mu$ s after the electron pulse. The characteristic spectrum of CF<sub>2</sub> was observed. At this time there is no adduct left (see Figure 7A), and it seems reasonable

 $k_{-5} \, [s^{-1}]$ 

 $(8.3 \pm 2.5) \times 10^5$ 

 $(9.4 \pm 1.5) \times 10^{5}$ 



 $k_5 \text{ [cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{]}$ 

 $(1.56\pm 0.31)\times 10^{-11}$ 

 $(1.25\pm 0.25)\times 10^{-11}$ 

**Figure 9.** Absorbance following radiolysis of 20 mbar of CF<sub>2</sub>BrH and 980 mbar of SF<sub>6</sub>. The spectrum was recorded  $100-101 \ \mu s$  after the electron pulse. The sharp absorption lines are due to CF<sub>2</sub> radicals.



**Figure 10.** Transient absorbance at 249 nm 50  $\mu$ s after the electron pulse versus the relative dose. Mixtures of 5 mbar of CF<sub>2</sub>BrH and 980 mbar of SF<sub>6</sub> were radiolysed.

to assume that  $CF_2$  is formed from decomposition of the adduct via reaction 7.

Figure 7B displays the transient absorption at 249 nm following the radiolysis of a mixture of 995 mbar SF<sub>6</sub> and 5 mbar of CF<sub>2</sub>BrH. The dose was 42% of maximum, and the optical path length was 80 cm. At 249 nm CF<sub>2</sub> radicals absorb strongly, and it is seen in Figure 7B that the absorption does not fall to zero within the observed time interval, this is ascribed to the formation of CF<sub>2</sub> radicals. CF<sub>2</sub> radicals are relatively unreactive and are expected to be persistent in the reaction cell over a time scale of the order of  $10^{-4}$  s. A series of experiments was performed where the radiolysis dose was varied over an order of magnitude. As shown in Figure 7A, at 50 us after the radiolysis pulse the loss of adduct is essentially complete. Figure 10 shows a plot of the absorbance 50  $\mu$ s after the electron pulse versus the relative dose. The solid line is a linear least squares fit to the low dose data. The slope is  $\beta = (0.61 \pm$ 0.04). The yield of  $CF_2$  relative to the amount of  $[F]_0$  was



Figure 11. UV spectrum of the  $CF_2BrH$ --F adduct. The spectrum of the  $CH_3Br$ --F adduct is shown for comparison.

calculated from the expression  $[CF_2]/[F_0] = \beta 2.303/(\sigma(CF_2)-[F]_0)$ , where  $[F]_0 = 3.2 \times 10^{15}$  molecule cm<sup>-1</sup> and l = 80 cm is the optical path length. Unfortunately, the literature values of  $\sigma(CF_2)$  differ considerably:  $\sigma_{249nm}(CF_2) = (2.9 \pm 0.4) \times 10^{-17}$ ,<sup>16</sup>  $\sigma_{249nm}(CF_2) = (8.0 \pm 1.4) \times 10^{-18}$ ,<sup>17</sup> and  $\sigma_{249nm}(CF_2)$ =  $(8.4 \pm 0.4) \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup>.<sup>18</sup> From these values the yield of CF<sub>2</sub> was calculated to be 19%, 69%, or 65%, respectively. Quantification of the CF<sub>2</sub> yield is further complicated by the fact that  $\sigma_{249nm}(CF_2)$  is sensitive to the internal excitation of the CF<sub>2</sub> radical.<sup>18</sup> The internal excitation of the CF<sub>2</sub> radicals observed here is unknown. Therefore, we are unable to provide a precise quantification of the substantial CF<sub>2</sub> yield.

**3.6.** UV Absorption Spectrum of the Adduct X. The absolute cross section of the adduct X was determined at 280 nm from the experiments described in section 3.1. The absorption cross section was determined from the expression  $\sigma = 2.303\alpha(1 + K_5[CF_2BrH])/(lK_5[CF_2BrH][F]_0)$ , where  $\alpha$  is the slope of a linear regression fit to the data shown in Figure 2, l = 120 cm, and  $[F]_0 = 3.2 \times 10^{15}$  molecules cm<sup>-3</sup> is the F atom yield at full radiolysis dose. The results were  $\sigma = (1.35 \pm 0.15) \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> from experiments with [CF\_2BrH] = 20 mbar and  $\sigma = (1.16 \pm 0.13) \times 10^{-17}$  from experiments with [CF\_2BrH] = 2.5 mbar.

The UV absorbance spectrum of the adduct X following the pulsed irradiation of a mixture of 20 mbar of CF2BrH and 980 mbar of SF<sub>6</sub> was measured using a diode array. The conditions were as follows: spectral resolution = 3 nm, wavelength = 230–380 nm, gate =  $1-2 \mu s$ , 53% of full radiolysis dose. To place the observed UV absorption of the adduct on an absolute basis the absorptions were scaled to that at 280 nm and converted into absolute absorption cross sections using  $\sigma(280\text{nm})$ =  $1.3 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup>. The spectrum of the adduct is shown in Figure 11, and the absorption cross sections are given in Table 2. The overall uncertainty in the absorption cross sections is estimated to be 25% and arises from uncertainty in the F atom yield, the equilibrium constant, and the stability in the lamp pulse used to record the spectrum. In Figure 11 a spectrum of the adduct formed in the reaction of F atoms with CH<sub>3</sub>Br<sup>19</sup> is shown for comparison. As seen from Figure 11, the spectra of the two adducts are almost identical suggesting that they have similar structure.

# 4. FTIR Results and Discussion

4.1. FTIR Study of the Reaction of Cl Atoms with CF<sub>2</sub>BrH. A series of relative rate experiments was performed

 TABLE 2: Selected UV Absorption Cross Sections for the

 CF2BrH-F Adduct

v

vavelength	$10^{20}\sigma$	wavelength	$10^{20}\sigma$
(nm)	$(cm^2 molecule^{-1})$	(nm)	(cm <sup>2</sup> molecule <sup>-1</sup> )
230	466	310	1012
240	795	320	682
250	985	330	437
260	977	340	266
270	1051	350	163
280	1290	360	94
290	1482	370	53
300	1334	380	18
Ln([CF <sub>2</sub> BrH] <sub>t0</sub> /[CF <sub>2</sub> BrH] <sub>t</sub> )	.6 CI .4 CI .2 CI 0.0 0.4 0 Ln([Methane	)4 <b>8</b> 1.2 ] <sub>t0</sub> /[Methar	CH <sub>4</sub> 1.6 2.0 ne] <sub>t</sub> )

Figure 12. Loss of  $CF_2BrH$  versus loss of methane when  $CF_2BrH$ / methane mixtures were exposed to Cl atoms in 700 Torr of air diluent.

using the FTIR system to investigate the kinetics and mechanism of the reaction of Cl atoms with CF<sub>2</sub>BrH. The techniques used are described in detail elsewhere.<sup>20</sup> Photolysis of molecular chlorine was used as a source of Cl atoms:

$$Cl_2 + h\nu \rightarrow 2Cl$$
 (8)

$$Cl + CF_2BrH \rightarrow CF_2Br + HCl$$
 (9)

The kinetics of reaction 9 were measured relative to reactions 10 and 11. The observed losses of  $CF_2BrH$  versus  $CD_4$  and

$$Cl + CD_4 \rightarrow CD_3 + DCl \tag{10}$$

$$Cl + CH_4 \rightarrow CH_3 + HCl$$
 (11)

CH<sub>4</sub> following the UV irradiation of CF<sub>2</sub>BrH/CD<sub>4</sub>/Cl<sub>2</sub> and CF<sub>2</sub>BrH/CH<sub>4</sub>/Cl<sub>2</sub> mixtures, respectively, in 700 Torr total pressure of air diluent are shown in Figure 12. Linear leastsquares analysis gives  $k_9/k_{10} = 0.89 \pm 0.05$  and  $k_9/k_{11} = 0.061$  $\pm$  0.005. Using  $k_{10} = 6.1 \times 10^{-15}$  (ref 20) and  $k_{11} = 1.0 \times 10^{-15}$  $10^{-13}$  (ref 21) gives  $k_9 = (5.4 \pm 0.3) \times 10^{-15}$  and  $k_9 = (6.1 \pm 0.3) \times 10^{-15}$  $(0.5) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. We choose to cite a final value for  $k_9$  which is the average of the two experimental determinations with error limits which encompass the extremes of the determinations. Hence,  $k_9 = (5.8 \pm 0.8) \times$  $10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. We estimate that potential systematic errors associated with uncertainties in the reference rate constants could add an additional 10% to the uncertainty range. Propagating this additional 10% uncertainty gives  $k_9 = (5.8 \pm$ 1.0) × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. While there is no literature available for  $k_9$  for direct comparison, our result is of the order of magnitude expected for reaction of Cl atoms with a halomethane containing two F substituents.<sup>22</sup>



**Figure 13.** Formation of  $COF_2$  versus the loss of  $CF_2BrH$  observed following the Cl atom (circles) or F atom (triangles) initiated oxidation of  $CF_2BrH$  in 700 Torr of air diluent.

Figure 13 shows a plot of the observed formation of  $COF_2$  versus the loss of  $CF_2BrH$  following UV irradiation of a mixture of 9.2 mTorr of  $CF_2BrH$  and 174 mTorr of  $CI_2$  in 700 Torr of air. Linear least-squares analysis of the data in Figure 13 gives a molar yield of  $COF_2$  of  $100 \pm 4\%$ .  $COF_2$  was the only carbon-containing product observed. By analogy to the behavior of other peroxy radicals<sup>22</sup> it is expected that the self-reaction of  $CF_2BrO_2$  radicals proceeds to give the corresponding alkoxy radicals, which will then eliminate a Br atom to give  $COF_2$ :

$$CF_2BrO_2 + CF_2BrO_2 \rightarrow CF_2BrO + CF_2BrO + O_2$$
 (12)

$$CF_2BrO + M \rightarrow CF_2O + Br$$
 (13)

The experimental observation that Cl-initiated oxidation of  $CF_2BrH$  in our system gives 100% yield of  $COF_2$  is entirely consistent with the expected behavior. In addition to the experiments performed in air, two experiments were performed to investigate the products following the UV irradiation of  $CF_2BrH/Cl_2/N_2$  mixtures. The initial  $CF_2BrH$  concentration was 12.3 mTorr, the  $Cl_2$  concentration was either 2.7 or 10.4 Torr, and  $N_2$  was added to give a total pressure of 700 Torr.

CF<sub>2</sub>BrCl was the major product following UV irradiation of CF<sub>2</sub>BrH/Cl<sub>2</sub> mixtures, in yields of  $88 \pm 4\%$  and  $94 \pm 4\%$  from experiments employing 2.7 and 10.4 Torr of Cl<sub>2</sub>, respectively. In addition to CF<sub>2</sub>BrCl, one or more unknown products were observed with infrared features at 793, 831, 923, 1093, 1153, and 1161 cm<sup>-1</sup>. Trace amounts of COF<sub>2</sub> were also detected by virtue of its characteristic feature at 774 cm<sup>-1</sup>. The observed products can be rationalized in terms of the following reactions:

$$CF_2BrH + Cl \rightarrow CF_2Br + HCl$$
 (9)

$$CF_2Br + Cl_2 \rightarrow CF_2BrCl + Cl$$
 (14)

$$CF_2Br \rightarrow \rightarrow products$$
 (15)

Reaction 15 represents an unknown loss mechanism for  $CF_2Br$  radicals. The increase in  $CF_2BrCl$  yield with increasing  $Cl_2$  concentration reflects a competition between reactions 14 and 15 for the available  $CF_2Br$  radicals. The trace of  $COF_2$  reflects the presence of a small amount of  $O_2$  in the 700 Torr of  $N_2$  diluent, and so reactions 2, 12, and 13 play a small role.

At this point it is germane to consider the thermochemistry of reaction 9. By comparison to structurally similar molecules, we estimate the C–Br bond and C–H bond strengths in CF<sub>2</sub>BrH



Figure 14. Loss of  $CF_2BrH$  versus loss of  $CF_3CFH_2$  and  $CF_3CH_3$  when  $CF_2BrH/CF_3CFH_2$  and  $CF_2BrH/CF_3CH_3$  mixtures were exposed to F atoms in 700 Torr of either air (filled symbols) or N<sub>2</sub> (open symbols) diluent.

to be 72 and 104 kcal mol<sup>-1</sup>, respectively.<sup>23</sup> The bond strengths in Br–Cl and H–Cl are 52 and 103 kcal mol<sup>-1</sup>, respectively. Hence, H atom abstraction is the only thermodynamically allowed channel of the reaction of Cl atoms with CF<sub>2</sub>BrH. The experimental results discussed above are consistent with the expectation that CF<sub>2</sub>Br radicals are formed in 100% yield from reaction 9. In light of the adduct formation between F atoms and CF<sub>2</sub>BrH, it seems likely that Cl atoms also form an adduct with CF<sub>2</sub>BrH. From the present work we cannot discern whether formation of CF<sub>2</sub>Br radicals in reaction 9 occurs via concerted H-atom abstraction or via the intermediacy of a CF<sub>2</sub>BrH–Cl adduct which eliminates HCl.

**4.2. FTIR Study of the Reaction of F Atoms with CF<sub>2</sub>BrH.** To investigate the kinetics and mechanism of the reaction of F atoms with  $CF_2BrH$ , a series of relative rate experiments was performed using the FTIR system. Photolysis of molecular fluorine was used as a source of F atoms:

$$F_2 + h\nu \to 2F \tag{16}$$

$$F + CF_2BrH \rightarrow products$$
 (4)

The kinetics of reaction 4 were measured relative to reactions 17 and 18. The observed losses of  $CF_2BrH$  versus  $CF_3CFH_2$ 

$$F + CF_3 CFH_2 \rightarrow CF_3 CFH + HF$$
(17)

$$F + CF_3CH_3 \rightarrow CF_3CH_2 + HF$$
(18)

and CF<sub>3</sub>CH<sub>3</sub> following the UV irradiation of CF<sub>2</sub>BrH/CF<sub>3</sub>CFH<sub>2</sub>/ F<sub>2</sub> and CF<sub>2</sub>BrH/CF<sub>3</sub>CH<sub>3</sub>/F<sub>2</sub> mixtures, respectively, in 700 Torr total pressure of N<sub>2</sub> or air diluent are shown in Figure 14. Linear least-squares analysis gives  $k_4/k_{17} = 0.67 \pm 0.06$  and  $k_4/k_{18} =$  $0.40 \pm 0.04$ . The reactivity of both CF<sub>3</sub>CFH<sub>2</sub> and CF<sub>3</sub>CH<sub>3</sub> toward F atoms has been the subject of recent investigations in our laboratories.<sup>15,24</sup> Using  $k_{17} = 1.3 \times 10^{-12}$  (ref 15) and  $k_{18} =$  $2.3 \times 10^{-12}$  (ref 24) gives  $k_4 = (8.7 \pm 0.8) \times 10^{-13}$  and  $k_4 =$  $(9.2 \pm 0.9) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. We choose to cite a final value for  $k_4$  which is the average of the two experimental determinations with error limits which encompass the extremes of the determinations. Hence,  $k_4 = (9.0 \pm 1.1) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. We estimate that potential systematic errors associated with uncertainties in the reference rate constants could add an additional 20% to the uncertainty

TABLE 3: Observed Product Yields (percent) following Radiation of  $F_2/CF_2BrH/N_2$  Mixtures

[CF <sub>2</sub> BrH][F <sub>2</sub> ]	11.5 mTorr	11.5 mTorr	11.5mTorr
	0.444 Torr	1.92 Torr	3.8 Torr
$[COF_2]$	$53 \pm 4$	$14 \pm 4$	$15 \pm 3$
	9 + 1	64 + 6	70 ± 6
$[CF_3Br]$	$8\pm 2$	$16 \pm 3$	$16 \pm 6$
[CF <sub>3</sub> O <sub>3</sub> CF <sub>3</sub> ] total C	$5 \pm 1 \\ 80 \pm 9$	$^{<2}$ 94 ± 13	$^{<2}$ 101 ± 11

range. Propagating this additional 20% uncertainty gives  $k_4 = (9.0 \pm 2.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

While there are no literature data to compare with this result, we can compare the value of  $k_4 = (9.0 \pm 2.1) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> obtained using the FTIR system with the value expected on the basis of results from the pulse radiolysis experiments. As discussed in sections 3.4 and 3.5, the pulse radiolysis results show that the reaction proceeds via the formation of an adduct which is in dynamical equilibrium with F atoms and CF<sub>2</sub>BrH. In addition to decomposition into reactants, the adduct is also lost via a process which follows pseudo-first-order kinetics to give products other than F atoms and CF<sub>2</sub>BrH:

$$F + CF_2BrH \rightleftharpoons X$$
 (5,-5)

 $X \rightarrow \text{products}$  (7)

The reactivity of F atoms toward CF<sub>2</sub>BrH determined by the FTIR technique was derived by comparing the loss of CF<sub>2</sub>BrH to that of a reference compound whose reactivity toward F atoms is known. Hence, the FTIR technique is "blind" to any reaction channel which leads to reformation of CF2BrH within the experimental time scale (minutes). The "effective" rate constant measured by the FTIR method is then  $K_5k_7$ . Using the values of  $K_5 = (1.59 \pm 0.13) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$  and  $k_7 = (7.4)^{-17} \text{ cm}^3 \text{ molecule}^{-1}$  $\pm$  0.7)  $\times$  10<sup>4</sup> s<sup>-1</sup> from the pulse radiolysis study, it would be predicted that the "effective" rate constant measured by the FTIR method would be  $(1.2 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The value measured by the FTIR, (9.0  $\pm$  2.1)  $\times$  10<sup>-13</sup> cm<sup>3</sup> molecule $^{-1}$  s $^{-1}$ , is in excellent agreement with the value predicted by the pulse radiolysis experiments. This agreement supports the assumption made in section 3.1 that direct hydrogen abstraction makes a negligible contribution to the reaction of F atoms with CF<sub>2</sub>BrH. The kinetic data obtained using the pulse radiolysis and FTIR techniques provide a consistent picture of the reaction of F atoms with CF2BrH proceeding essentially via the formation of an adduct. Under the present experimental conditions, 1 atm at 296 K, the predominant fate of the CF<sub>2</sub>BrH--F adduct is decomposition to reactants. A small fraction (8%) of the adduct decomposes into products.

To provide further insight into the mechanism of reaction 5, experiments were performed using the FTIR smog chamber in which CF<sub>2</sub>BrH/F<sub>2</sub> mixtures in 700 Torr of either air or N<sub>2</sub> diluent were subject to UV irradiation. COF<sub>2</sub> was the only carboncontaining product observed following UV irradiation of  $CF_2BrH/F_2$  mixtures in air diluent. The formation of  $COF_2$  is plotted versus the loss of CF<sub>2</sub>BrH in Figure 13. The results obtained using F atom initiated oxidation of CF<sub>2</sub>BrH in air are indistinguishable from those obtained using Cl atom initiation, with COF<sub>2</sub> formed in essentially 100% yield. Three experiments were performed in which F<sub>2</sub>/CF<sub>2</sub>BrH mixtures at a total pressure of 700 Torr made up with N<sub>2</sub> diluent were irradiated and the loss of CF<sub>2</sub>BrH and the formation of products were monitored by FTIR spectroscopy. Experimental conditions are given in Table 3. Figure 15 shows the product yields with linear leastsquares analysis.



**Figure 15.** Product yields of  $CF_4(\bigcirc)$ ,  $CF_3Br(\blacktriangle)$ ,  $COF_2(\bigcirc)$ , and  $CF_{3}O_{3-}CF_{3}(\square)$  following irradiation of  $CF_2BrH/F_2/N_2$  mixtures. The experimental details are given in the text and in Table 3.

Four carbon-containing products were observed following UV irradiation of CF<sub>2</sub>BrH/F<sub>2</sub>/N<sub>2</sub> mixtures; CF<sub>4</sub>, CF<sub>3</sub>Br, COF<sub>2</sub>, and CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub>. In all product studies care must be taken to ensure that the reactant compound is lost only via the reaction of interest and that the products are not lost via secondary reactions. To assess possible heterogeneous and photolytic loss in the chamber, CF<sub>2</sub>BrH/air and CF<sub>3</sub>Br/air mixtures were prepared, allowed to stand for 20 min, then irradiated for 20 min; no loss (<1%) of CF<sub>2</sub>BrH or CF<sub>3</sub>Br was discernible. It has been established previously that COF<sub>2</sub> and CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub> are not subject to loss via heterogeneous reactions, photolysis, or reaction with F atoms.<sup>25</sup> Finally, CF<sub>2</sub>BrH/CF<sub>3</sub>Br/F<sub>2</sub>/air mixtures were subject to UV irradiation to check for reaction of F atoms with CF3Br. In such experiments loss of CF<sub>2</sub>BrH was observed but there was no loss (<1%) of CF<sub>3</sub>Br, showing that the CF<sub>3</sub>Br is not consumed in this system via reaction with F atoms (F atoms may react with CF<sub>3</sub>Br, but if so, the adduct must decompose to reform CF<sub>3</sub>Br resulting in no overall loss of this compound). As seen from Table 3, the yields of CF<sub>4</sub> and CF<sub>3</sub>Br increased, while those of COF<sub>2</sub> and CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub> decreased, with increasing  $[F_2]_0$ . CF<sub>3</sub>Br and COF<sub>2</sub> formation can be rationalized by the formation of CF2Br radicals via overall hydrogen atom abstraction from CF<sub>2</sub>BrH followed by reaction either with F<sub>2</sub> or with O<sub>2</sub> impurity in the chamber to give CF<sub>3</sub>Br or CF<sub>2</sub>BrO<sub>2</sub> radicals. The CF<sub>2</sub>BrO<sub>2</sub> radicals are then converted into COF<sub>2</sub> via reactions 12 and 13:

$$CF_2BrH + F \rightarrow CF_2Br + HF$$
 (4a)

$$CF_2Br + F_2 \rightarrow CF_3Br + F$$
 (19)

$$CF_2Br + O_2 \rightarrow CF_2BrO_2$$
 (2)

The formation of  $CF_4$  and  $CF_3O_3CF_3$  shows that a substantial fraction of the reaction of F atoms with  $CF_2BrH$  proceeds via

a mechanism other than simple hydrogen abstraction. There is only one reaction that can form  $CF_3O_3CF_3$  in the chamber, namely

$$CF_3O + CF_3O_2 \rightarrow CF_3O_3CF_3 \tag{20}$$

 $CF_3O_2$  and  $CF_3O$  radicals are formed following reaction of  $CF_3$ radicals with  $O_2$ . The detection of  $CF_3O_3CF_3$  as a minor product shows that  $CF_3$  radicals are formed. The  $CF_4$  product may also reflect the formation of  $CF_3$  radicals in the chamber and their subsequent reaction with  $F_2$ :

$$CF_3 + F_2 \rightarrow CF_4 + F \tag{21}$$

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$$
(22)

At 296 K and 700 Torr total pressure  $k_{21} = 7.0 \times 10^{-14}$  (ref 26) and  $k_{22} = 3.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>27</sup> Hence,  $k_{22}/k_{21} = 50$ . For the conditions of experiment no. 1 (see Table 3) and assuming all the CF<sub>4</sub> is attributable to reaction 21, then the O<sub>2</sub> impurity is present at a concentration which is 2.2% of the F<sub>2</sub>, i.e., 9.9 mTorr. The presence of such a small amount of O<sub>2</sub> from a combination of incomplete evacuation, leaks of air into the chamber, and/or the presence of O<sub>2</sub> in the reactant gases is not unreasonable.

## 5. Discussion

The pulse radiolysis experiments described in section 3 demonstrate that the reaction of F atoms with CF<sub>2</sub>BrH proceeds substantially via the formation of an adduct, CF<sub>2</sub>BrH--F, which at 296 K decomposes rapidly to regenerate CF<sub>2</sub>BrH and F atoms and to give other products. Let us consider how the results obtained using the FTIR smog chamber system fit in with this picture. Several consistent points emerge. First, the observation of loss of CF<sub>2</sub>BrH following UV irradiation of CF<sub>2</sub>BrH/F<sub>2</sub> mixtures shows that either not all of the reaction gives the adduct, or not all of the adduct decomposes to regenerate the initial reactants, or both. Second, the observation of CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub> products cannot be explained if the reaction of F atoms with CF<sub>2</sub>BrH proceeded via a simple hydrogen abstraction mechanism. There are several thermodynamically feasible decomposition pathways for the adduct:

$$CF_2BrH--F \rightarrow CF_2BrH+F$$
 (-5)

$$CF_2BrH--F \rightarrow CF_2Br + HF$$
  $\Delta H = -32 \text{ kcal mol}^{-1}$ 
(23)

$$CF_2BrH--F \rightarrow CF_2 + Br + HF \qquad \Delta H = +3 \text{ kcal mol}^{-1}$$
(24)

 $CF_2BrH$ --F $\rightarrow CF_3Br$ +H  $\Delta H = -13 \text{ kcal mol}^{-1}$  (25)

 $CF_2BrH--F \rightarrow CF_3 + HBr$   $\Delta H = -30 \text{ kcal mol}^{-1}$  (26)

 $CF_2BrH--F \rightarrow CF_3H + Br \qquad \Delta H = -49 \text{ kcal mol}^{-1}$  (27)

The heats of reaction above were derived using  $\Delta H_f(CF_3) = -111$  kcal mol<sup>-1</sup>,<sup>28</sup>  $\Delta H_f(CF_2BrH) = -109$  kcal mol<sup>-1</sup>,  $\Delta H_f(CF_2Br) = -57$  kcal mol<sup>-1</sup> (estimated by interpolation of literature data for CF<sub>3</sub>H and CBr<sub>3</sub>H, and CF<sub>3</sub> and CBr<sub>3</sub><sup>23</sup>), and  $\Delta H_f(CF_2BrH-F) = -90$  kcal mol<sup>-1</sup> (assumed, for the sake of argument, equal to  $\Delta H_f(CF_2BrH) + \Delta H_f(F)$ ). Let us consider these possibilities in turn and assess their likely importance based upon the experimental observations presented herein. As discussed in sections 3.2–3.5, the evidence from the pulse

radiolysis experiments shows that decomposition to reactants (pathway -5) is the main fate of the adduct. The question then is which of the remaining possibilities account for that fraction of the adduct loss which is not simple decomposition into reactants. The results from the FTIR study shed some light on this issue. CF<sub>3</sub>H is relatively unreactive toward F atoms<sup>15</sup> and, if formed in the FTIR experiments, will not be lost via secondary reactions. The absence of any observable CF<sub>3</sub>H shows that pathway 27 is of no importance. For those experiments employing the largest [F<sub>2</sub>]<sub>0</sub>, CF<sub>4</sub> was the dominant product accounting for up to 70% of the CF<sub>2</sub>BrH loss. Pathways 23 and 25 lead indirectly (via the  $CF_2Br + F_2$  reaction) or directly to CF<sub>3</sub>Br and not CF<sub>4</sub>, so it appears these pathways are, at most, of minor importance. Pathway 26 leads to CF<sub>4</sub> formation via reaction of the CF<sub>3</sub> radical with F<sub>2</sub> and so could be important. In the presence of 700 Torr of air, CF3 radicals are converted essentially quantitatively into CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub>.<sup>25</sup> The observation of 100% yield of COF2 in CF2BrH/F2/air experiments shows that in 700 Torr of air diluent pathway 26 is not a significant loss of the adduct, i.e., if reaction 26 is responsible for the observed CF<sub>4</sub> in the N<sub>2</sub> experiments, then there must be a reaction of the adduct with O<sub>2</sub> to give directly, or indirectly, COF<sub>2</sub> in the experiments conducted in air diluent.

In the pulse radiolysis experiments we have shown that the decomposition of the adduct gives a substantial (20–72%) yield of CF<sub>2</sub> radicals. Hence, we conclude that pathway 24, although slightly endothermic, is of importance. There is insufficient kinetic data concerning the chemistry of CF<sub>2</sub> radicals to predict their behavior in the FTIR smog chamber experiments. It is conceivable that in the presence of 2–4 Torr of F<sub>2</sub> the CF<sub>2</sub> radicals react to give CF<sub>4</sub>, but in the presence of trace amounts of air they react to give COF<sub>2</sub> exclusively.

## 6. Conclusion

Halogen atom adducts have been observed in solution; see, for example, refs 29-31. These adducts are described as charge-transfer complexes according to the Mulliken theory.<sup>32</sup> We present here a large body of self-consistent kinetic and mechanistic data which shows that the reaction of F atoms with CF<sub>2</sub>BrH gives an adduct in the gas phase. The adduct is in dynamic equilibrium with CF<sub>2</sub>BrH and F atoms. The adduct can also decompose to CF<sub>2</sub> radicals and other products. Further work is needed to assess if this novel reaction mechanism is important in reaction of F atoms with other brominated compounds.

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