Kinetics and Mechanism of the Reaction of F Atoms with CH₃Br

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The reaction of F atoms with CH₃Br at 296 K was studied using a pulse radiolysis/transient UV absorption spectroscopy absolute technique and a FTIR relative rate technique. The rate constant for this reaction was determined to be $(4.46 \pm 0.22) \times 10^{-11}$. The reaction proceeds via two channels, $69 \pm 5\%$, via hydrogen abstraction giving CH₂Br radicals and HF, and $31 \pm 5\%$, to give the adduct CH₃Br--F. In the FTIR system the observed rate constant was $69 \pm 8\%$ of that measured using the pulse radiolysis system because the CH₃Br--F adduct falls apart to re-form the reactants. The CH₃Br--F adduct reacts with NO, with a rate constant of $(2.25 \pm 0.14) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, giving FNO as a product. There was no discernible reaction of the CH₃Br--F adduct with O₂ and an upper limit of 6×10^{-15} cm³ molecule⁻¹ s⁻¹ was derived for this reaction. The CH₃Br--F adduct absorbs strongly at 260-340 nm. The absorption cross section at 280 nm of the CH₃Br--F]/([CH₃Br][F]) > 5×10^{-16} cm³ molecule⁻¹ at 296 K. A lower limit of 12 kcal mol⁻¹ is estimated for the binding energy of the F atom in the CH₃Br--F adduct. The UV absorption spectrum of the CH₂BrO₂ radical was determined; at 250 nm $\sigma = (3.4 \pm 0.9) \times 10^{-18}$ cm² molecule⁻¹.

1. Introduction

Recognition of the adverse impact of bromine compounds on stratospheric ozone has led to interest in the atmospheric chemistry of CH_3Br .¹ It is believed that there are two major sources of atmospheric CH_3Br : an anthropogenic source from its use as a fumigant and a natural source from the oceans.² The overall source strength is estimated to be 100-150 kT/year. It is estimated that up 30% of the CH_3Br release could be of anthropogenic origin.² The observed atmospheric concentration is $10-15 \text{ ppt.}^2$

The principal removal mechanism for CH₃Br in the atmosphere is reaction with OH:

$$CH_{3}Br + OH \rightarrow CH_{2}Br + H_{2}O$$
(1)

The lifetime of CH₃Br in the atmosphere with respect to reaction 1 is approximately 1.8 years.^{2–5} Reaction 1 produces CH₂Br radicals which then add oxygen rapidly (within 1 μ s) to give peroxy radicals.^{6,7}

$$CH_2Br + O_2 + M \rightarrow CH_2BrO_2 + M$$
 (2)

As with other peroxy radicals in the atmosphere, CH_2BrO_2 radicals are expected to react with NO, NO₂, HO₂, and other

peroxy radicals (R'O₂):⁸⁻¹⁰

$$CH_2BrO_2 + NO \rightarrow CH_2BrO + NO_2$$
 (3a)

$$CH_2BrO_2 + NO + M \rightarrow CH_2BrONO_2 + M$$
 (3b)

$$CH_2BrO_2 + NO_2 + M \rightleftharpoons CH_2BrO_2NO_2 + M$$
 (4, -4)

$$CH_2BrO_2 + HO_2 \rightarrow products$$
 (5)

$$CH_2BrO_2 + R'O_2 \rightarrow products$$
 (6)

There have been two previous studies of the UV spectra and kinetics of CH_2Br and CH_2BrO_2 radicals. The first study was performed in our laboratory and employed the reaction of F atoms with CH_3Br as a source of CH_2Br and hence CH_2BrO_2 radicals.⁶ The second study was performed by Villenave and Lesclaux⁷ and used the reaction of Cl atoms with CH_3Br to generate CH_2Br radicals. The spectroscopic and kinetic results from these two studies are in substantial disagreement, suggesting that different radical species were present in the two studies. The goal of the present work was to understand this discrepancy.

Recent results from our laboratory show that an adduct is formed in the reaction of F atoms with CF₂BrH¹¹ and that this

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adduct is in equilibrium with the reactants, F atoms and CF_2 -BrH:

$$F + CF_2BrH \rightleftharpoons CF_2BrH--F$$
 (7, -7)

Less than 1% of the reaction of F atoms with CF_2BrH at ambient temperature proceeds via direct hydrogen abstraction to give CF_2Br radicals and HF.¹¹ The formation of a short-lived molecular complex in the reactions of Cl atoms with CH_3I and CH_3Br has also been reported recently by Wine et al.¹²

In the present work we present kinetic and spectroscopic data which show that the reaction of F atoms with CH₃Br proceeds via two reaction channels: adduct formation and direct hydrogen abstraction. Formation of the CH₃Br--F adduct via channel 8a explains the discrepancy between the previous studies of the UV spectra and kinetics of CH₂Br and CH₂BrO₂ radicals. Spectral and kinetic information for the CH₃Br--F adduct and CH₂BrO₂ radical are presented herein.

$$F + CH_3Br \rightleftharpoons CH_3Br - F$$
 (8a, -8a)

$$F + CH_3Br \rightarrow CH_2Br + HF \tag{8b}$$

2. Experimental Section

The two experimental systems used in the present work have been described in detail previously 1^{13-15} and will only be discussed briefly here.

2.1. Pulse Radiolysis Setup. A pulse radiolysis transient UV absorption apparatus was used to study the UV absorption spectra and kinetics of the CH2Br radical and the CH3Br--F adduct. Radicals were generated by radiolysis of gas mixtures at 296 K in a 1 L stainless steel reactor by a 30 ns pulse of 2 MeV electrons from a Febetron 705B field emission accelerator. The radiolysis dose, expressed throughout this article as a fraction of maximum dose, was varied by insertion of stainless steel attenuators between the accelerator and the chemical reactor. The analyzing light was obtained from a pulsed Xenon arc lamp and reflected in the reaction cell by internal White type optics. The optical path lengths used in this work were 80 and 120 cm. The analyzing light was monitored by a 1 m McPherson monochromator linked to a Hamamatsu R928 photomultiplyer and a LeCroy 9450A oscilloscope. The monochromator was operated at a spectral resolution of 0.8 nm when the photomultiplier was applied as the detection method. All transients were results of single-pulse experiments with no signal averaging.

A Princeton Applied Research OMA-II diode array was used to measure UV absorption spectra of transient species. 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. The spectral resolution of the diode array spectra of the CH₃Br--F adduct and the CH₂-BrO₂ radical was 3.2 nm. The spectral resolution applied for the FNO spectra was 0.8 nm.

 SF_6 was used as the diluent gas, the radiolysis of SF_6 is known to produce fluorine atoms:¹³

$$SF_6 + (2 \text{ MeV})e^- \rightarrow F + \text{ products}$$
 (9)

 SF_6 was always present in great excess to minimize the relative importance of direct radiolysis of other compounds in the gas mixtures. The fluorine atom yield, required for quantification

of UV absorption spectra, was calculated from the observed absorbance at 260 nm due to CH₃O₂ radicals formed upon radiolysis of mixtures of CH₄, O₂, and SF₆ using σ_{260nm} (CH₃O₂) = (3.18 ± 0.32) × 10⁻¹⁸ cm² molecule^{-1.9} The fluorine atom yield was (3.0 ± 0.3) × 10¹⁵ molecules cm⁻³ (full dose, 1000 mbar SF₆). The quoted uncertainty reflects propagation of a 10% uncertainty in σ (CH₃O₂) and the statistical uncertainty (2 standard deviations) of the absorbance at 260 nm.

Reagents used were as follows: O₂ (ultrahigh purity), 0-110 mbar; SF₆ (99.9%), 885–1000 mbar; CH₃Br (>99%), 0-20 mbar; NO (>99.8%), 0-2.5 mbar; and CH₄ (>99%), 0-10 mbar. O₂ was supplied by L'Air Liquide. SF₆, CH₃Br, and CH₄ were obtained from Gerling and Holz. NO was provided by Messer Griesheim. All reagents were used as received.

2.2. FTIR–**Smog Chamber Setup.** The FTIR system was interfaced to a 140 l Pyrex reactor. Radicals were generated by the UV irradiation of mixtures of CH₃Br, CH₄, CD₄, and F₂ in N₂ or air diluent, at 296 K using 22 black lamps (760 Torr = 1013 mbar). The loss of reactants was monitored by FTIR spectroscopy, using an analyzing path length of 26 m and an optical resolution of 0.25 cm⁻¹. Infrared spectra were acquired by expanding known volumes of reference materials into the reactor. All reagents were supplied by Michigan Air Gas at >99% purity. Ultrahigh purity N₂ or air diluents were used.

All uncertainties reported in this paper are 2 standard deviations unless otherwise stated. Standard error propagation methods are used to calculate combined uncertainties.

3. Results

3.1. Kinetics of the Reaction of F Atoms with CH₃Br. Radicals were generated by radiolysis of mixtures of 0.5-2.16 mbar of CH₃Br and 1000 mbar of SF₆:

$$SF_6 + (2 \text{ MeV})e^- \rightarrow F + \text{products}$$
 (9)

$$F + CH_3Br \rightarrow products$$
 (8)

Following the radiolysis pulse a rapid increase in absorption at 280 nm was observed, followed by a slower decay. An experimental transient recorded at 280 nm using 11% of the maximum radiolysis dose, 80 cm UV path length, and a mixture of 0.79 mbar of CH_3Br and 1000 mbar of SF_6 is shown in Figure 1A. The absorption transients such as that shown in Figure 1A were fitted using a first order rise expression:

$$A(t) = (A_{\infty} - A_0)(1 - \exp(-k^{1st}t)) + A_0$$
 (I)

where A(t), A_0 , and A_{∞} are the absorbance as function of time t, at time zero, and at infinite time, respectively. $k^{1\text{st}}$ is the pseudo-first order formation rate equal to k_8 [CH₃Br]. The values of $k^{1\text{st}}$ obtained are plotted as a function of the initial CH₃Br pressure in Figure 2. A linear least squares regression gives $k_8 = (4.46 \pm 0.22) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

There is a small positive intercept in Figure 2 of $(9.9 \pm 6.6) \times 10^4 \text{ s}^{-1}$. This intercept can be explained by the loss of the absorbing radical species. A dose of 0.11 was used to obtain the data plotted in Figure 2. The decay lifetime of the absorbance at 280 nm under these conditions was approximately 20 μ s and was independent of [CH₃Br]. This gives a pseudo-first order decay rate of 5.0 × 10⁴ s⁻¹. Using this decay rate, $k_8 = 4.46 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹, and the CHEMSIMUL¹⁶ numerical integration program, simulated transients were calculated for [CH₃Br] = 0.5 and 2.16 mbar. The calculated transients were fitted using the first order first expression (I) given above, and the values of $k^{1\text{st}}$ obtained are plotted in Figure



Figure 1. Transient absorption at 280 nm following radiolysis of (A) a mixture of 0.79 mbar of CH_3Br and 1000 mbar of SF_6 , dose 0.11, and (B) a mixture of 2.5 mbar of CH_3Br and 1000 mbar of SF_6 , dose 0.32. The UV path length was 80 cm. The smooth line in A is a first order fit to the experimental data. See text for details.



Figure 2. First order formation rate constants (filled circles) following pulse radiolysis of mixtures of 0.5–2.16 mbar of CH₃Br and 1000 mbar of SF₆ plotted as a function of [CH₃Br]. Measurements were made at 280 nm. The slope of the straight line through the data is $(4.66 \pm 0.22) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹. The hollow circles are the results of computer simulations. See text for details.

2 as open circles. As seen from the figure, the decay of the transients explain the small intercept in Figure 2 and therefore no correction is needed for this complication. The value of k_8



Figure 3. Loss of CH_3Br versus CH_4 (triangles), CF_2HCH_3 (152a) (circles), and CD_4 (diamonds) when mixtures containing these compounds were exposed to F atoms in 700 Torr of air diluent.

= $(4.46 \pm 0.22) \times 10^{-11}$ obtained here is in good agreement with the value obtained previously by Nielsen et al.⁶ of $(4.5 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

The kinetics of the reaction of F atoms with CH_3Br were also studied by a FTIR relative rate technique.

3.2. FTIR Relative Rate Study of the Reaction of F Atoms with CH₃Br. To investigate the kinetics of the reaction of F atoms with CH₃Br, relative rate studies were performed using the FTIR system. The techniques used are described in detail elsewhere.^{17,18} Photolysis of molecular fluorine was used as a source of F atoms. The kinetics of reaction 8 were measured relative to reactions 11-13. Figure 3 shows the observed losses

$$F_2 + h\nu \to 2F \tag{10}$$

$$F + CH_3Br \rightarrow products$$
 (8)

$$F + CHF_2CH_3$$
 (HFC-152a) $\rightarrow CHF_2CH_2 + HF$ (11)

$$F + CH_4 \rightarrow CH_3 + HF \tag{12}$$

$$F + CD_4 \rightarrow CD_3 + DF \tag{13}$$

of CH₃Br versus those of the reference compounds following irradiation of mixtures of CH3Br/CHF2CH3/F2, CH3Br/CH4/F2, and CH₃Br/CD₄/F₂ in 700 Torr of air diluent. Linear least squares analyses gives $k_8/k_{11} = 1.87 \pm 0.14, k_8/k_{12} = 0.51 \pm$ 0.03, and $k_8/k_{13} = 0.79 \pm 0.04$. The reactivity of F atoms toward CHF₂CH₃ and CD₄ relative to that of CH₄ are $k_{11}/k_{12} =$ 0.25 ± 0.02^{-18} and $k^{13}/k_{12} = 0.69 \pm 0.02^{-19}$ These rate constant ratios can be combined with the determinations of $k_8/k_{11} = 1.87$ \pm 0.14 and $k_8/k_{13} = 0.79 \pm 0.04$ in the present work to provide values of $k_8/k_{12} = 0.47 \pm 0.05$ and 0.55 ± 0.04 . Errors were propagated using conventional error analysis. It is gratifying to note the internal consistency of the relative rate data. We choose to quote the direct measurement of $k_8/k_{12} = 0.51 \pm 0.03$ as the final value. Using $k_{12} = 6.8 \times 10^{-11}$ to place this measurement on an absolute basis gives $k_8 = (3.47 \pm 0.20) \times$ $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Potential systematic errors associated with uncertainty in the reference rate constant could add an additional 20% to the uncertainty range. Propagating this additional uncertainty gives $k_8 = (3.47 \pm 0.72) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹.



Figure 4. Maximum transient absorbance at 280 nm following radiolysis of 20 mbar (filled circles) or 2.5 mbar (hollow circles) of CH₃Br and 990 mbar of SF₆. The slope of the straight line through the low-dose data (dose < 0.53) is 0.652 ± 0.013 .

3.3. Investigation of the Radical Yield as Function of Radiolysis Dose. Determination of the absolute UV absorption cross sections of the radical species formed in the reaction of F atoms with CH3Br requires accurate quantification of the radical concentrations. If we assume that only one absorbing species is formed, we need to know the initial F atom yield and the fraction of the F atoms that is converted into the absorbing species. It is important to choose experimental conditions which avoid unwanted radical-radical reactions such as F + CH₂Br and F + F, which could otherwise interfere with stoichiometric conversion of F atoms into the desired radical species. To check for unwanted chemistry, the maximum transient absorption was measured as a function of the radiolysis dose. In Figure 4 the maximum transient absorbance at 280 nm is plotted as a function of the dose. As seen from the figure, the absorbance is proportional to the radiolysis dose up to a relative dose of 0.53 for $[CH_3Br]_0 = 20$ mbar and 0.42 for $[CH_3Br]_0 = 2.5$ mbar. This linearity indicates that for low radiolysis doses radicalradical reactions and other loss mechanisms for the absorbing species do not interfere significantly with its formation.

Two initial pressures of CH₃Br were used, 2.5 and 20 mbar. The slope of the straight line through the low-dose data (dose 0.53 and lower for $[CH_3Br]_0 = 20$ mbar and dose 0.42 and lower for $[CH_3Br]_0 = 2.5$ mbar) at 280 nm is 0.652 \pm 0.013. In the following experiments a dose of 0.53 was used to avoid unwanted radical-radical reactions.

An observed value of the absorption cross section at 280 nm can be calculated using (i) the slope of the straight line through the data points in Figure 4, 0.652 \pm 0.013, (ii) the UV path length of 80 cm, and (iii) the initial F atom yield of $(3.0 \pm 0.3) \times 10^{15}$ molecules cm⁻³. The absorption cross section at 280 nm is $(6.26 \pm 0.64) \times 10^{-18}$ cm² molecule⁻¹. The quoted error includes both the statistical uncertainty from the plot in Figure 4 and uncertainty in the initial F atom yield. It is important to stress here that the absorption cross section derived above is only an observed absorption cross section for a mix of radicals and not for a specific species.

3.4. Composite Spectrum of the Radicals Formed from the $F + CH_3Br$ Reaction. The UV spectrum of the species formed in the reaction of F atoms with CH_3Br was recorded using the diode array following radiolysis of mixtures of 2.5 mbar of CH_3Br and 1000 mbar of SF_6 . In these experiments the time delay between the radiolysis pulse and data acquisition



Figure 5. Composite spectrum of the products following the reaction of F atoms with CH_3Br (adduct and CH_2Br). Spectra of CH_2Br of Villenave and Lesclaux⁷ (hollow circles) and Nielsen et al.⁶ (filled circles) are shown for comparison. The straight line in the [CH₃-Br--F] spectrum is an extrapolation between two spectra.

was 1 μ s, the integration time was 1 μ s, the relative dose was 0.53, and the UV path length was 80 cm. To place the spectrum on an absolute basis, the absorbance at 280 nm was scaled to the observed absorption cross section determined above. The spectrum is plotted in Figure 5. The spectra of CH₂Br radicals reported by Nielsen et al.⁶ and Villenave and Lesclaux⁷ are also plotted in Figure 5. As seen from the figure, at wavelengths greater than 250 nm the diode array spectrum is in reasonable agreement with that attributed by Nielsen et al.⁶ to CH₂Br radicals. The reason for this apparent discrepancy at wavelengths below 250 nm is probably scattered light of higher wavelengths. Measurements at wavelengths of 240 nm and below are difficult in this system because CH3Br absorbs at these wavelengths, $\sigma(230 \text{nm}) = 1.5 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1.20}$ The Hilger and Watts monochromator used by Nielsen et al.⁶ had a lower discrimination toward scattered light than the presently used McPherson monochromator. We therefore believe that the spectrum obtained in this work upon the reaction of F atoms with CH₃Br is plausibly the same as that reported by Nielsen et al.⁶

Clearly, the spectra obtained from the reaction of F atoms with CH_3Br and the spectrum of CH_2Br radicals reported by Villenave and Lesclaux⁷ are very different. Villenave and Lesclaux⁷ used the reaction of Cl atoms with CH_3Br to generate CH_2Br radicals:

$$Cl + CH_3Br \rightarrow CH_2Br + HCl$$
 (14)

The inconsistency between the spectra using Cl atoms and F atoms to produce CH_2Br radicals can be explained in light of recent results from our laboratory which show that F atoms and CF_2BrH form an adduct which is in equilibrium with the reactants:¹¹

$$F + CF_2BrH \rightleftharpoons CF_2BrH--F$$
 (7, -7)

The equilibrium constant was determined to be $K_{eq} = (1.59 \pm 0.12) \times 10^{-17} \text{ cm}^3$ molecule⁻¹. The spectrum of this adduct is shown in Figure 10. As seen from Figures 5 and 10 the absorption spectrum of the CF₂BrH--F adduct in the region of 260–340 nm is similar to that of the radical products of the reaction of F atoms with CH₃Br. This suggests that a substantial



Figure 6. Maximum transient absorption at 280 nm following pulse radiolysis of mixtures of 0-100 mbar of CH₄, 5 mbar of CH₃Br, and 1000 mbar of SF₆. The solid line is a fit to the data. See text for details.

fraction of reaction 8 proceeds via a mechanism which involves formation of an adduct:

$$F + CH_3Br \rightleftharpoons CH_3Br - F$$
 (8a, -8a)

$$F + CH_3Br \rightarrow CH_2Br + HF$$
 (8b)

Further evidence suggesting that an adduct is formed in the reaction of F with CH_3Br is presented in the following subsections.

3.5. Determination of $k(F+CH_3Br)$ Relative to $k(F+CH_4)$. The rate of the reaction of F atoms with CH₃Br was measured relative to that of F atoms with CH₄. When mixtures of 5 mbar of CH₃Br, 0–100 mbar of CH₄, and 1000 mbar of SF₆ are subject to pulse radiolysis, there is a competition for the F atoms between CH₃Br and CH₄:

$$F + CH_3Br \rightarrow products$$
 (8)

$$F + CH_4 \rightarrow CH_3 + HF \tag{12}$$

Figure 6 shows the observed variation of the maximum transient absorbance at 280 nm as a function of the concentration ratio $[CH_4]/[CH_3Br]$. As seen from the figure, the maximum transient absorption at 280 nm decreases with increasing CH₄ concentration. The decrease in absorbance at 280 nm can be rationalized in terms of the competition between reactions 8 and 12 for the F atoms. At high CH₄ pressures, CH₃ radicals are formed at the expense of F + CH₃Br reaction products. CH₃ radicals do not absorb at 280 nm. Therefore the maximum transient absorbance decreases with increasing amounts of CH₄.

The competition between reactions 8 and 12 can be used to determine k_8/k_{12} as follows. The data in Figure 6 can be fitted with a three parameter expression:

$$A_{\max} = \{A_{F+CH_3Br} + (A_{F+CH_4}[CH_4]/((k_8/k_{12})[CH_3Br]))\}/(1 + [CH_4]/((k_8/k_{12})[CH_3Br]))$$

where A_{max} , $A_{\text{F+CH}_4}$, and $A_{\text{F+CH}_3\text{Br}}$ are the observed maximum absorbance as a function of the ratio [CH₄]/[CH₃Br], the absorbance if all F atoms react with CH₄, and the absorbance if all F atoms react with CH₃Br. $A_{\text{F+CH}_4}$, $A_{\text{F+CH}_3\text{Br}}$, and k_8/k_{12} were simultaneously varied, and the best fit was achieved with $k_8/k_{12} = 0.74 \pm 0.08$. Using $k_{12} = (6.8 \pm 1.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹,²¹ we arrive at $k_8 = (5.0 \pm 1.1) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, in good agreement with the value of $(4.46 \pm 0.22) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ determined using the pulse radiolysis technique described in section 3.1.

The measurement of k_8 relative to k_{12} is interesting for three reasons: First, it is a complementary determination of k_8 in our system and agrees with the other pulse radiolysis determination. Second, the fact that we get the same value of k_8 strongly indicates that the absorbance at 280 nm is attributable to some product of the reaction of F atoms with CH₃Br. If another radiolysis product were responsible for the absorbance at 280 nm, it is extremely unlikely that this species has the same relative reaction rate with CH₄ and CH₃Br as F atoms. Third, it is interesting to note that the value of k_8/k_{12} derived here (0.74 \pm 0.08) is significantly different from $k_8/k_{12} = 0.51 \pm 0.03$, derived by the FTIR relative rate method described in section 3.2. The apparent discrepancy in values of k_8 determined by the pulse radiolysis and FTIR techniques can be rationalized if we consider two factors: first, the different time scales employed by the two techniques; second, the mechanism for the reaction of F atoms with CH₃Br which proceeds at least in part via the formation of an adduct which can decompose back to reactants.

$$F + CH_3Br \rightleftharpoons [CH_3Br--F] \rightarrow products$$
 (8a, -8a, 15)

$$F + CH_3Br \rightarrow CH_2Br + HF$$
 (8b)

Reaction 15 represents unimolecular processes which remove the adduct without reformation of F atoms or CH₃Br. Reactions 8a and 8b remove F atoms on the time scale of the pulse radiolysis experiments (0–100 μ s). If reaction –8a is much faster than reaction 15, then only reaction channel 8b will remove F atoms on the time scale of the FTIR experiments (5-10 min). In the case of the CF₂BrH--F adduct, less than 10% of the adduct decomposition lead to products other than F and CF₂BrH.¹¹ Assuming reaction 15 is negligible, the fraction of F atoms that react via reaction channel 8b is $(0.51 \pm 0.03)/$ $(0.74\pm0.08)=0.69\pm0.08.~$ This suggests that 31% of the F atoms react via channel 8a and 69% via channel 8b. The determination of $k_{8a}/k_8 = 31 \pm 8\%$ should be regarded as a lower limit as reaction 15 may compete with reaction -8a. At this point it is worth noting that decomposition of the CF₂BrH--F adduct proceeds essentially entirely (>90%) to regenerate CF₂BrH and F atoms.¹¹ In light of the behavior of the CF₂-BrH--F adduct it seems reasonable to assume that the determination of $k_{8a}/k_8 = 31 \pm 8\%$ is not a gross underestimate. In the following section we investigate the reaction of the complex with NO to confirm the value for the branching determined here.

3.6. Reaction of the CH₃Br--F Adduct with NO. Mixtures of 0–2.5 mbar of NO, 5–20 mbar of CH₃Br, and SF₆ added to 1000 mbar were radiolyzed, and the absorbance at 230 and 280 nm were recorded. The decay rate of the transient absorbance at these wavelengths increased with increasing NO concentration. The decays were fitted with a first order decay expression, and first order decay rates were derived. In Figure 7, first order decay rates are plotted as a function of [NO]. The slopes of the straight lines through the data give rate constants of (2.25 \pm 0.08) × 10⁻¹¹ (filled circles, 280 nm) and (2.16 \pm 0.41) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ (hollow triangles, 230 nm). The intercepts are due to the self-reactions and cross-reactions of the radicals.

CH₂Br radicals do not absorb significantly at 280 nm.⁷ Therefore the decay rate determined from the absorbance decay



Figure 7. First order decay rates at 280 nm (filled circles) and 230 nm (hollow triangles) as a function of [NO] following radiolysis of mixtures of 0-2.5 mbar of NO, 5-20 mbar of CH₃Br, and 990 mbar of SF₆.

at 280 nm is the rate constant for reaction 16. Hence, $k_{16} =$

$$CH_3Br-F + NO \rightarrow products$$
 (16)

 $(2.25 \pm 0.08) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. We choose to add an extra 5% uncertainty due to systematic uncertainties and hence report $k_{16} = (2.25 \pm 0.14) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. It is shown below that the CH₃Br--F adduct absorbs less than the CH₂Br radical at 230 nm. Therefore, we conclude that the rate constant derived from the decay at 230 nm is close to rate constant for reaction 17. Hence, k_{17} approximately equals (2.16

$$CH_2Br + NO \rightarrow products$$
 (17)

 \pm 0.41) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. We conclude that both the CH₃Br--F adduct and the CH₂Br radical react with NO with rate constants of approximately 2.2 \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹.

What are the products of reactions 16 and 17? By analogy with the reaction of other alkyl radicals with NO we expect that the product of reaction 17 is CH_2BrNO . The likely products of reaction 16, if we regard CH_3Br --F as a molecular complex with the F atom loosely bound, are FNO and CH_3Br .

To investigate the formation of FNO from reaction 16, two chemical systems were subject to pulse radiolysis: (i) a mixture of 10 mbar of NO and 990 mbar of SF_6 and (ii) a mixture of 20 mbar of CH_3Br , 2.5 mbar of NO, and 997.5 mbar of SF_6 . In reaction mixture i the following reactions are important:

$$SF_6 + (2 \text{ MeV})e^- \rightarrow F + \text{products}$$
 (9)

$$F + NO + M \rightarrow FNO + M \tag{18}$$

The transient absorbance 100 μ s after the electron pulse is shown in Figure 8A. The formation of FNO is complete ($k_{18} = 5.1 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ ^{22,23}) 100 μ s after the radiolysis pulse. The two peaks at 308 and 311 nm are well-known FNO features.²⁴ The absorbance following the radiolysis of reaction mixture ii is shown in Figure 8B. Clearly, FNO is also formed in system ii. It seems reasonable to conclude that FNO is formed via reaction 16. The ratio of the amount of FNO formed in experiments ii and i gives us the ratio of k_{8a}/k_8 . The FNO yield was determined by subtraction of spectrum A from B. In Figure 8 the residual spectra following the subtraction of 22,



Figure 8. Diode array spectra 100–100.2 μ s after radiolysis of mixtures of (A) 10 mbar and 990 mbar of SF₆ and (B) 2.5 mbar of NO, 20 mbar of CH₃Br, and 980 mbar of SF₆. C–E are residual spectra obtained by subtracting 22, 27, and 32% of spectrum A from spectrum B, respectively. For clarity 0.01, 0.02, and 0.03 was subtracted from C–E, respectively. Full-dose and 120 cm UV path length were used.



Figure 9. Maximum transient absorbance at 310.5 nm following radiolysis of mixtures of 10 mbar of NO and 990 mbar of SF₆ (filled squares) and 2.5 mbar of NO, 20 mbar of CH₃Br, and 977.5 mbar of SF₆ (circles). The straight lines are linear regressions of the filled data points.

27, and 32% of spectrum A from spectrum B are shown. It is evident from the figure that the FNO yield in reaction mixture ii is $27 \pm 5\%$ of that in reaction mixture i.

Two corrections are needed before a final value of k_{8a}/k_8 can be derived. First, some F atoms are lost because a full radiolysis dose was used to derive the spectrum of mixture ii. In Figure 9 the maximum transient absorbance at 310.5 nm is plotted as a function of the radiolysis dose following radiolysis of reaction mixtures i and ii. The maximum transient absorbance is proportional to the dose over the entire range tested for reaction mixture i. This indicates that F atoms are converted quantitatively into FNO. This is not the case for reaction mixture ii. The full-dose absorbance (0.0304) falls below the extrapolation of the low-dose data (0.0355). This indicates that radicals are lost by secondary chemistry. The amount of FNO expected if secondary chemistry was absent relative to the amount of FNO actually formed is 0.0355/0.0304 = 1.17. We estimate the uncertainty on this correction to be 10%. The corrected yield of FNO is then = $(0.27 \pm 0.05) \times (1.17 \pm 0.12) = 0.32 \pm$ 0.07.



Figure 10. Spectra of the CH₃Br--F adduct (this work) and the CF₂-BrH--F adduct.¹¹ The straight line in the [CH₃Br--F] spectrum is a extrapolation between two spectra.

The second correction stems from the fact that 1.4% of the F atoms react directly with NO via reaction 18. The value of 1.4% was calculated from the initial concentrations of CH3Br (20 mbar) and NO (2.5 mbar) and $k_{18} = 5.1 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ 22,23 and $k_8 = 4.46 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Application of this final correction gives $k_{8a}/k_8 = 0.31 \pm 0.07$. This value is in excellent agreement with the value of 0.31 \pm 0.08 derived in section 3.5. The value determined from the reaction of the CH₃Br--F adduct with NO could potentially be lower than the real value, if the reaction gives products other than FNO and CH₃Br. However, it seems likely that reaction 16 gives 100% FNO and CH₃Br because the F atom in the adduct is expected to be only weakly bound and thus removed easily by NO. While the determination of $k_{8a}/k_8 = 0.31 \pm 0.07$ in this section and that of $k_{8a}/k_8 = 0.31 \pm 0.08$ given in section 3.5 should be strictly viewed as lower limits, the excellent agreement between these two independent methods suggests that these determinations are close to the actual value of k_{8a}/k_8 . Hence, we choose to report a value of k_{8a}/k_8 of $\{(0.31 \pm 0.07)\}$ $+ (0.31 \pm 0.08) \frac{1}{2} = 0.31 \pm 0.05.$

3.7. UV Absorption Spectrum of the CH₃Br--F Adduct. We are now in a position to calculate the UV absorption spectrum of the CH₃Br--F adduct using three pieces of information: (i) the observed UV spectrum determined in this work, (ii) the branching $k_{8a}/k_8 = 0.31 \pm 0.05$, and (iii) the UV absorption spectrum of CH₂Br radicals reported by Villenave and Lesclaux.⁷ The formula $\sigma([CH_3Br--F]) = (\sigma(\text{observed}) - 0.69\sigma(CH_2Br))/0.31$ was used where $\sigma(CH_3Br--F)$ is the absorption cross section at a given wavelength of the CH₃Br--F adduct, $\sigma(\text{observed})$ is the observed spectrum following the reaction of F atoms with CH₃Br (see Figure 5), and $\sigma(CH_2Br)$ is the CH₂-Br spectrum reported by Villenave and Lesclaux⁷ (see Figure 5). The spectrum of the adduct derived using this approach is



Figure 11. Reciprocal of the decay half-life at 280 nm plotted as a function of the maximum transient absorbance at 280 nm. The straight line is a linear regression.

plotted in Figure 10, and the absorption cross sections are listed in Table 1. Also listed in Table 1 is the uncertainty calculated by a conventional error propagation method using 15% uncertainty in σ (observed), k_{8a}/k_8 , and σ (CH₂Br). As seen from Figure 10 the absorption spectrum of the CH₃Br--F adduct is similar to the spectrum reported for the CF₂BrH--F adduct.¹¹

3.8. Decay of the CH₃Br--F Adduct. Figure 1B shows an experimental absorption transient recorded at 280 nm following radiolysis of a mixture of 2.5 mbar of CH₃Br and 1000 mbar of SF₆. In Figure 11, $1/t_{1/2}$ is plotted as a function of the maximum transient absorbance at 280 nm. The maximum absorbance was varied by varying the radiolysis dose. As seen from Figure 11, the decay rate increased linearly with radical concentration (higher absorbance). This indicates that radical-radical reactions such as

$$CH_3Br-F + CH_2Br \rightarrow products$$
 (19)

$$CH_3Br-F + CH_3Br-F \rightarrow products$$
 (20)

$$CH_3Br-F+F \rightarrow products$$
 (21)

dominate removal of the CH₃Br--F adduct. The slope of the straight line through the data in Figure 11, $(8.9 \pm 0.7) \times 10^5$ s⁻¹, is a measure of the speed of such radical-radical reactions. However, it is a measure of a mixture of reactions 19–21, and we will not pursue this further. The intercept in Figure 11 is $(0.85 \pm 1.24) \times 10^4$ s⁻¹ and contains important information regarding the equilibrium between F atoms, CH₃Br, and the CH₃-Br--F adduct.

TABLE 1: Selected UV Absorption Cross Sections with Uncertainties for the CH₃Br--F Adduct

	$\sigma imes 10^{20}$ (cm ² molecule)			$\sigma \times 10^{20} (\mathrm{cm^2 \ molecule^{-1}})$	
wavelength (nm)	σ(CH ₃ BrF)	$\Delta\sigma(CH_3Br-F)$	wavelength (nm)	σ(CH ₃ BrF)	$\Delta \sigma$ (CH ₃ BrF)
230	140	400	320	945	140
240	640	390	330	645	95
250	1125	265	340	418	63
260	1280	205	350	263	40
270	1775	238	360	156	22
280	2055	310	370	100	16
290	2140	319	380	73	13
300	1830	270	390	51	8
310	1300	190	400	29	5

There are two possible first order loss mechanisms for the CH_3Br --F adduct. These are via reactions -8a and 15.

$$F + CH_3Br \rightleftharpoons CH_3Br--F \rightarrow products$$
 (8a, -8a, 15)

$$F + CH_3Br \rightarrow CH_2Br + HF$$
 (8b)

Decomposition via reaction -8a gives F atoms and CH₃Br. The F atoms then react again with CH₃Br; 31% re-form the adduct, while 69% do not re-form the adduct. Hence, the observed decay rate (intercept in Figure 11) could be interpreted as being 69% of k_{-8a} . The intercept in Figure 11 gives $k_{-8a} < 2.1 \times 10^4$ ((ln 2)/0.69) s⁻¹, i.e., $<2.1 \times 10^4$ s⁻¹. This is slower than the decomposition rate of the CF₂BrH--F adduct of (9 ± 3) × 10⁵ s⁻¹ determined by Bilde et al.,¹¹ suggesting that the CH₃-Br--F adduct is more strongly bound than the CF₂BrH--F adduct.

Decomposition via reaction 15 does not regenerate F atoms, and the intercept in Figure 11 gives an upper limit of $k_{15} < 2.1 \times 10^4 \ln 2 \text{ s}^{-1} = 1.5 \times 10^4 \text{ s}^{-1}$. This can be compared with the analogous decomposition rate of the CF₂BrH--F adduct which is $(7.4 \pm 0.7) \times 10^4 \text{ s}^{-1}$. The CH₃Br--F adduct is more stable than the CF₂BrH--F adduct, both toward decomposition into F atoms and the parent compound and other products.

 k_{8a} can be calculated from $k_{8a}/k_8 = 0.31 \pm 0.05$ and the overall rate constant of reaction 8, $k_8 = (4.46 \pm 0.22) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. $k_{8a} = (1.4 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. This rate is, within the error limits, equal to the rate for the addition of F atoms to CF₂BrH of $(1.5 \pm 0.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The similarity in their formation kinetics and UV spectra (see Figure 10) suggests that the adducts formed by the reaction of F atoms with CF₂BrH and CH₃Br are similar in nature.

A lower limit for the equilibrium constant for the CH₃Br--F adduct can be calculated from the k_{8a} , and k_{-8a} values using $K_{eq} = k_{8a}/k_{-8a} > 6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$. This should be compared with the equilibrium constant for the CF₂BrH--F adduct of $(1.6 \pm 0.1) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$. The CH₃Br--F adduct is more stable than the CF₂BrH--F adduct.

3.9. Reaction of CH₃Br--F Adduct with O₂ and the Spectrum of CH₂BrO₂. Three mixtures containing 5 mbar of CH₃Br, 950 mbar of SF₆, and either 0, 50, or 110 mbar of O₂ were subject to pulse radiolysis (32% of maximum dose), and the transient absorption at 280 nm was recorded. The decay half-lives of the absorbance transients were 6.0, 6.8, and 6.8 μ s. The shorter half-life in the absence of O₂ could indicate that the CH₃Br--F adduct reacts with CH₂Br radicals but does not react, or reacts only slowly, with O₂. If we assume a 10% error limit on the decay half-lives above, the upper limit for the rate constant of the reaction of the CH₃Br--F adduct with O₂ is {(ln 2)/(6.8 μ s) - (ln 2)/(6.8 μ s)}/(110-50 mbar) = 6 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹.

The CH₂BrO₂ radical is expected to be formed upon radiolysis of mixtures of CH₃Br/O₂/SF₆ by the reaction of CH₂Br radicals with O₂:

$$CH_2Br + O_2 + M \rightarrow CH_2BrO_2 + M$$
 (22)

The UV absorption spectrum of CH₂BrO₂ was recorded using the diode array $30-35 \ \mu s$ after radiolysis (53% of maximum dose) of mixtures of 5 mbar of CH₃Br, 50 mbar of O₂, and 945 mbar of SF₆. The UV path length was 80 cm. The absorption is shown in the insert in Figure 12. The reason for delaying the data acquisition $30-35 \ \mu s$ after the pulse is to allow time for the rapid decay of the CH₃Br--F adduct. The decay of the CH₂BrO₂ radical is expected to be slow since the self-reaction rate constant of CH₂BrO₂ radicals determined by Villenave and



Figure 12. Spectrum of CH_2BrO_2 determined in this work. The spectrum of CH_2BrO_2 reported by Villenave and Lesclaux⁷ (filled circles) is shown for comparison. The insert shows the absorbance following radiolysis of a mixture of 5 mbar of CH_3Br , 50 mbar of O_2 , and 945 mbar of SF₆ (upper curve). The two low-absorbance curves in the insert are the absorbance due to FO₂ (maximum at 230 nm) and the CH₃Br-F adduct (maximum at 290 nm). See text for details.

Lesclaux is 1.05×10^{-12} cm³ molecule⁻¹ s^{-1.7} Using the absorbance shown in the insert in Figure 12, the UV absorption spectrum of CH₂BrO₂ can be determined. Three corrections are necessary to extract the spectrum of CH₂BrO₂ from the observed spectrum. (i) The spectrum has to be corrected for the absorption due to the CH₃Br--F adduct. The absorbance at 280 nm of the CH₃Br--F adduct in this system 33 μ s after the electron pulse is approximately 0.03 absorbance units; see Figure 1B. The UV absorption spectrum of the CH₃Br--F adduct given in Figure 10 was scaled to an absorbance of 0.03 at 280 nm to give the result shown in the insert in Figure 12 which was then subtracted from the observed absorbance spectrum. (ii) Also shown in the insert in Figure 12 is the absorbance of FO₂ formed in the system using the absorption cross sections reported by Ellermann et al.²⁵ The fraction of F atoms that is converted into FO₂ can be calculated using $k(F+O_2) = 1.9 \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹,²⁵ $k_8 = 4.46 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, and the initial concentrations of CH₃Br, 5 mbar, and O₂, 50 mbar. The fraction of F atoms that is converted into FO₂ radicals is 4%. The fraction of F atoms that forms CH₂Br radicals is then $0.69 \times 0.96 = 0.66$. (iii) Finally, we need a correction due to the self-reaction of the CH₂BrO₂ radical. Using a F atom yield at full dose of 3 \times 10^{15} molecules cm $^{-3},$ 53% of full dose, a conversion factor for the F atoms into CH₂BrO₂ radicals of 0.66, and the self-reaction rate constant for CH2BrO2 radicals reported by Villenave and Lesclaux,⁷ we calculate that 7% of the CH₂- BrO_2 radicals are lost in the 33 μ s between radical formation and radical detection.

The spectrum can now be calculated from the corrected absorbance, the initial fluorine atom yield of 3×10^{15} cm⁻³, 53% of maximum dose, the UV path length of 80 cm, and the fraction of F atoms converted into CH₂Br radicals, 0.66, using the following formula: σ (CH₂BrO₂) = absorbance/(80 cm × 3 × 10¹⁵ cm⁻³ × 0.66 × 0.53). The spectrum of the CH₂BrO₂ radical is shown in Figure 12, and selected absorption cross sections are listed in Table 2. The spectrum of CH₂BrO₂ reported by Villenave and Lesclaux⁷ is shown in Figure 12 for comparison. It is seen from the figure that the spectrum of Villenave and Lesclaux.⁷ We estimate the overall uncertainty on the absorption cross section of CH₂BrO₂ to be 25%.

 TABLE 2:
 Selected UV Absorption Cross Sections for the

 CH₂BrO₂ Radical
 CH₂BrO₂ Radical

	$\sigma imes 10^{20}$		$\sigma imes 10^{20}$
wavelength	(cm ² molecule ⁻¹)	wavelength	(cm ² molecule ⁻¹)
(nm)	$\sigma(CH_2BrO_2)$	(nm)	$\sigma(CH_2BrO_2)$
230	345	270	172
240	377	280	100
250	341	290	52
260	261	300	24

Several potential reactions could interfere with the determination of the absorption spectrum of CH₂BrO₂ above:

$$F + CH_2Br/CH_3Br--F \rightarrow products$$
 (23)

$$CH_2Br + CH_2Br \rightarrow products$$
 (24)

$$CH_2Br + CH_3Br - F \rightarrow products$$
 (25)

$$CH_2BrO_2 + CH_3Br--F \rightarrow products$$
 (26)

$$F + CH_2BrO_2 \rightarrow products$$
 (27)

By analogy to the reaction of other alkyl radicals with $O_2^{8,10}$ the rate constant for the addition of O₂ to the CH₂Br radical is expected to be of the order of 3×10^{-12} cm³ molecule⁻¹ s⁻¹. Using this rate constant, the lifetime for CH₂Br radicals with respect to reaction with O_2 is 0.27 μ s. This should be compared with a lifetime for CH₂Br radicals and the CH₃Br--F adduct with respect to loss via self-reaction and cross reaction of approximately 5 μ s. Hence, reactions 24 and 25 are expected to be insignificant in the reaction system. The lifetime for the formation of CH₂Br radicals and CH₃Br--F adducts is 0.18 µs; thus, the influence of reaction 23 is negligible. Using the decay lifetime for F atoms and the formation lifetime of CH2BrO2 radicals and $k_{27} = 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in a numerical integration program, we estimate the loss of reactants to be <0.7% due to reaction 27. The significance of reaction 26, however, cannot be determined, since both the CH3Br--F adduct and the CH₂BrO₂ radical will be present in the system for several microseconds. Reaction (26) could be important. However, the excellent agreement between the spectrum of CH₂BrO₂ radicals reported here and the spectrum of Villenave and Lesclaux suggests that reaction 26 is not important.

The goal of the present series of experiments is not to remeasure the absorption spectrum of CH₂BrO₂ radicals but rather to understand the difference between the spectrum reported previously from our laboratory and that of Villenave and Lesclaux.⁷ The results reported herein show that, contrary to our initial expectations, the reaction of F atoms with CH₃Br does not proceed via a simple hydrogen atom abstraction mechanism but instead proceeds via two channels of which one produces an adduct which absorbs strongly in the UV. In the previous CH₂BrO₂ spectrum reported from this laboratory⁶ the absorption measured a few microseconds after the electron pulse were used to determine the spectrum of CH₂BrO₂. This spectrum includes absorption by the adduct because the adduct is not scavenged by O₂ and does not decay within a few microseconds. Figure 12 shows that when suitable corrections are applied to account for the formation of the CH₃Br--F adduct. the spectral data from the pulse radiolysis experiments can be reconciled with that of Villenave and Lesclaux.

4. Discussion and Conclusion

The kinetics and mechanism of the reaction of F atoms with CH3Br have been studied previously by Iyer and Rowland,^{26,27} Nielsen et al.,⁶ and Wallington et al.²¹ Iyer and Rowland were the first to study this reaction and reported that at 283 K in the presence of 3000 Torr of SF₆ diluent the reaction proceeds predominately via hydrogen atom abstraction with a small (0.27%) contribution by a direct displacement mechanism to give CH₃F and Br. The rate constant for hydrogen abstraction reported by Iyer and Rowland was (6.1 \pm 0.7) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Nielsen et al.⁶ used experimental techniques similar to those employed here and reported an overall rate constant for the reaction of F with CH3Br at 298 K in 1000 mbar of SF₆ diluent of $(4.5 \pm 0.9) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and an upper limit of 3% for the CH₃ radical yield. Nielsen et al.6 assumed that the reaction proceeded via hydrogen atom abstraction. Wallington et al.²¹ used a relative rate technique to derive $k(F+CH_3Br)/k(F+CH_4) = 0.44 \pm 0.03$ at 295 K in 700 Torr of air diluent. In the present work we show that at 296 K in 1000 mbar of SF₆ diluent reaction 8 proceeds with an overall rate constant of $(4.46 \pm 0.22) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} with 31% of the reaction giving an adduct and 69% giving $CH_2Br + HF$. In 700 Torr of air diluent we measure $k(F+CH_3-$ Br)/k(F+CH₄) = 0.51 \pm 0.03. The absolute value of k_8 measured here is consistent with that reported by Nielsen et al.⁶ but, for unknown reasons, is significantly lower than that measured by Iyer and Rowland.²⁷ The value of $k(F+CH_3Br)/$ $k(F+CH_4)$ determined using the FTIR method is slightly (16%) larger than the value reported by Wallington et al.²¹ This may reflect a slight underestimation of the CH₃Br loss in the previous work. In the present work two additional reference compounds were used (HFC-152a and CD₄), and the results from these references are more consistent with a ratio of $k(F+CH_3Br)/$ $k(F+CH_4) = 0.51 \pm 0.03$ than with a ratio of 0.44 ± 0.03 . Accordingly, we recommend that the present measurements supersede our previous determination.

The novel aspect of the present work is that it shows that reaction 8 proceeds via a two channel mechanism:

$$F + CH_3Br \rightleftharpoons CH_3Br - F$$
 (8a, -8a)

$$F + CH_3Br \rightarrow CH_2Br + HF$$
 (8b)

We have used this mechanism and the CH₂Br spectrum of Villenave and Lesclaux⁷ to derive the spectrum of the CH₃Br--F adduct. This spectrum is similar to the spectrum reported previously for the CF₂BrH--F adduct shown in Figure 11. In addition, the rate constants for addition of F atoms to CH₃Br, $(1.4 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and CF₂BrH, $(1.5 \pm$ 0.5) $\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, are, within the experimental uncertainties, indistinguishable. These reaction rates were measured both absolute and using relative techniques with consistent results. The stability of the CH₃Br--F adduct is greater than that of the CF₂BrH--F adduct. The equilibrium constant in the CH₃Br system is $k_{8a}/k_{-8a} > 5 \times 10^{-16} \text{ cm}^3$ molecule⁻¹, while the analogous equilibrium constant in the CF₂-BrH system is $(1.6 \pm 0.1) \times 10^{-17}$ cm³ molecule^{-1.11} It seems reasonable to assume that the entropy change in the formation of the CH₃Br--F and CF₂Br--F adducts is comparable. Hence, it can be concluded from the ratio of the equilibrium constants that the F atom in the CH₃Br--F adduct is bound by at least 2 kcal mol⁻¹ more than the CF₂BrH--F adduct. The estimated lower limit of the bond energy obtained from $k_{-8a} < 2.2 \times 10^4$ s^{-1} and $A_{-8a} > 10^{13} s^{-1}$ is $Ea_{-8a} > 12 kcal mol^{-1}$.

All evidence in the spectrokinetic study of the products of the reaction of F atoms with CH₃Br and CF₂BrH points toward formation of F adducts with the parent species. The question is: What is the nature of these species? Since F atoms form adducts with CH₃Br and CF₂BrH, it seems reasonable to suggest that in the adduct the F atom is bound to the bromine atom in the parent compound. One experimental observation appears to be in conflict with this conclusion; radiolysis of SF_6 in the presence of CF₃Br or CCl₃Br does not give significant absorption at 280 nm. Two potential explanations can be given for this. First, perhaps the formation of the adduct requires the presence of a Br atom and a H atom in the molecule. Therefore no adduct is formed from the reaction of F atoms with CF3Br or CCl₃Br. Second, perhaps the equilibrium constant for the equilibrium between F atoms and R-Br is shifted so much toward the left in the case of CF3Br and CCl3Br that we cannot observe the adduct formation in these cases. From the stability of the CH₃Br--F and CF₂BrH--F adducts, the stability of the complex seems to decrease when fluorine is present in the molecule. This trend is consistent with the inductive effect of the F atoms, reducing the electron density associated with the Br atom and hence reducing the adduct stability. This observation supports the suggestion made above that it is a lower equilibrium constant in the case of CF3Br and CCl3Br that leads to the failure in observing an adduct. From the absence of any detectable absorption and assuming that the CF₃Br--F and CCl₃-Br--F adducts have absorption cross sections at 280 nm which are comparable to those of CH₂Br--F and CF₂BrH--F, i.e., $1 \times$ 10^{-17} cm² molecule⁻¹, we provide estimates of 1×10^{-18} cm³ molecule⁻¹ for the upper limits of the equilibrium constants for the CF₃Br--F and CCl₃Br--F adducts at 296 K.

Further experimental studies of the reactions of F atoms with CF_3Br and CCl_3Br at low temperatures, the reaction of F atoms with other brominated compounds and theoretical calculations of the nature of the complexes are needed to provide more information on the structure of the adduct formed.

During the course of the present experiments Wine and coworkers reported evidence for the formation of adducts in the reactions of Cl atoms with CH₃Br and CH₃I.¹² It is possible that adduct formation is a common mechanism of the reaction of halogen atoms with haloalkanes. Further experimental and computational work is needed to explore this possibility.

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