Atmospheric Chemistry of CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, $CF_3CHBrCl$, and CBr_2Cl_2

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Relative-rate methods were used to measure the following rate constants at 296 K in 700 Torr of N_2, O_2, or air diluent (all cm^3 $molecule^{-1}$ s^{-1}): $k(OH + CHBrCl_2) = (1.2 \pm 0.3) \times 10^{-13}$, $k(OH + CH_2BrCl) = (1.2 \pm 0.3) \times 10^{-13}$, $k(Cl + CHBr_2Cl) = (2.2 \pm 0.6) \times 10^{-13}$, $k(Cl + CBr_2Cl_2) = (1.8 \pm 0.4) \times 10^{-13}$, $k(Cl + CBrCl_3) = (7.1 \pm 0.9) \times 10^{-14}$, and $k(Cl + CF_3CHBrCl) = (2.0 \pm 0.3) \times 10^{-14}$. Over the temperature range 217−296 K, $k(Cl + CHBrCl_2) = (2.6 \pm 0.4) \times 10^{-12} \exp(-852 \pm 76/T)$ and $k(Cl + CH_2BrCl) = (1.2 \pm 0.2) \times 10^{-11} \exp(-1000 \pm 82/T)$ cm^3 $molecule^{-1}$ s^{-1} were found. The UV absorption spectra of $CHBrCl_2$, $CF_3CHBrCl$, and $CHBr_2Cl$ were measured at temperatures between 223 and 298 K over the range 210−320 nm. The products of Cl-atom-initiated oxidation of $CHBrCl_2$, CBr_2Cl_2, $CHBr_2Cl$, and $CF_3CHBrCl$ were determined using FTIR smog-chamber techniques. Reaction of Cl atoms with $CHBrCl_2$, $CHBr_2Cl$, and $CF_3CHBrCl$ proceeds via hydrogen abstraction. Reaction of Cl atoms with CBr_2Cl_2 and $CBrCl_3$ occurs via bromine abstraction. Product studies of the Cl-initiated oxidation of $CHBrCl_2$ and CBr_2Cl_2 conducted with, and without, added NO showed strong evidence for the production of chemically activated alkoxy radicals in the reaction of $CBrCl_2O_2$ radicals with NO. These results are discussed with respect to the atmospheric chemistry of CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, CBr_2Cl_2, $CF_3CHBrCl$, and other brominated organic compounds.

1. Introduction

The release of bromine-containing organic compounds into the atmosphere is of interest because of their potential adverse impact on stratospheric ozone.[1] The major bromine-containing organics found in the free troposphere are CH_3Br, CH_2Br_2, $CBrF_3$, $CBrClF_2$, and $C_2Br_2F_4$,[2] with a total organic bromine concentration of 21 pptv near the tropopause at 24° N. A number of other species are also observed, including CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$, all of which appear to have natural oceanic sources[3−6], and $CF_3CHBrCl$, a man-made compound used as an anesthetic.[7,8] Assessment of the environmental impact of these species requires knowledge of the rates and mechanisms of their atmospheric removal processes, predominantly reaction with OH and photolysis.

The atmospheric oxidation of organic species occurs via the formation of alkyl peroxy radicals that react with NO to produce alkoxy radicals.[9] The subsequent fate of the alkoxy radical determines the first-generation atmospheric oxidation products. Recent studies of hydrofluorocarbon (HFC) oxidation have shown that reaction of alkyl peroxy radicals with NO can produce alkoxy radicals possessing internal excitation that is comparable to, or greater than, the barrier to C−C bond rupture.[10,11] These "hot" alkoxy radicals can decompose immediately and play an important role in dictating the nature of the atmospheric oxidation products. It is unclear whether this behavior is limited to alkoxy radicals formed from HFCs or whether it is a more general phenomenon. Alkoxy radicals formed in the oxidation of brominated and chlorinated methanes possess a variety of potentially accessible decomposition pathways (elimination of Br atoms,[12,13] Cl atoms,[14] HCl,[15,16] and potentially HBr), and thus might be prone to chemical-activation effects not recognized previously.

The aim of the present work is twofold. The first is to gather data useful in the determination of the atmospheric destruction rate of CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, and $CF_3CHBrCl$, including rates of reaction with Cl atoms (CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, $CF_3CHBrCl$), and OH radicals (CH_2BrCl and $CHBrCl_2$), and UV absorption spectra ($CHBrCl_2$, $CHBr_2Cl$, and $CF_3CHBrCl$). These data improve our understanding of the atmospheric lifetimes for these and related brominated compounds. The second is to study the mechanism of the oxidation

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of $CHBrCl_2$, $CHBr_2Cl$, and $CF_3CHBrCl$ to examine the behavior of chemically activated alkoxy radicals. As part of this work, a novel Br-atom-abstraction mechanism in the reaction of Cl atoms with CBr_2Cl_2 and $CBrCl_3$ is reported.

2. Experimental Section

Experiments were conducted using the environmental chambers at NCAR and Ford described previously.[17,18] The NCAR chamber was used to study the kinetics of reactions of Cl atoms with $CHBrCl_2$, CH_2BrCl, and $CF_3CHBrCl$, and OH radicals with CH_2BrCl and $CHBrCl_2$. The apparatus consists of a 2 m long, 47 L stainless steel temperature-regulated chamber interfaced to a Fourier transform spectrometer (BOMEM DA3.01) operating in the infrared. Multipass optics inside the reaction vessel provided a total absorption path length of 32.6 m. Cl atoms were generated by photolysis of molecular chlorine. OH radicals were generated by photolysis of O_3 in the presence of H_2O. The UV light source was a Xe arc lamp, with a Corning 7-54 filter (240−400 nm). Reactant loss and product formation were monitored by FTIR spectroscopy, using a resolution of 1 cm^{-1}. Infrared spectra were derived from 200 coadded spectra. Experiments were performed in 700 Torr total pressure of N_2, air, O_2, or He diluent. $CHBrCl_2$, CH_2Br_2, CH_2BrCl, $CF_3CHClBr$, and CH_4 were monitored using their characteristic features over the range 700−2000 cm^{-1}. Reagents were obtained at the highest purities available from commercial sources (ultrahigh purity for compressed gases and >99% for liquid samples). $CHBrCl_2$, CH_2Br_2, $CF_3CHClBr$, and CH_2BrCl were degassed by several freeze−pump−thaw cycles before use. All other chemicals were used as received.

The absorption cross section measurements were made using a diode-array spectrometer system.[19] The output of a D_2 lamp was collimated through an absorption cell (90-cm long, temperature-regulated Pyrex cell equipped with quartz windows) and focused into the entrance slit of a 0.3-m Czerny−Turner spectrograph equipped with a 300 groove/mm grating, which dispersed the light onto a diode-array detector. The system was calibrated using a low-pressure Hg penray lamp, and the spectral resolution was 0.6 nm. Absorption cross sections were obtained from the Beer−Lambert law $A(\lambda) = \ln[I_0(\lambda)/I(\lambda)] = \sigma lc$, where I_0 and I are the light intensity before and after addition of gas to the cell, respectively, l is the path length, and c is the concentration of the absorbing gas. Cross sections were determined at each wavelength from least-squares fits of plots of A/l versus c. To ensure accuracy and linearity, only absorbance values between 0.005 and 0.9 were used in the fits. Uncertainties are estimated to be ±4% at the peak of the spectra and ±35% at the longest wavelengths measured (due to the lower absorbances in this region).

The apparatus at Ford was used to study the kinetics of the reaction of Cl atoms with $CHBr_2Cl$, CBr_2Cl_2, and $CBrCl_3$ and products of the Cl-initiated oxidation of $CHBrCl_2$, $CHBr_2Cl$, and CBr_2Cl_2. The FTIR system was interfaced to a 140 L Pyrex reactor. Radicals were generated by the UV irradiation (22 black lamps) of molecular chlorine in the presence of one or more of the following species: $CHBrCl_2$, $CHBr_2Cl$, CBr_2Cl_2, $CBrCl_3$, CH_4, CD_4, CH_3F, CH_3Cl, CH_2D_2, ^{13}CO, and NO. All experiments were performed at 296 K in 700 Torr total pressure of air, N_2, or O_2 diluent. Reactant loss and product formation were monitored by FTIR spectroscopy, using an analyzing path length of 28 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 coadded spectra. A reference spectrum of $COCl_2$ was obtained from the reference library at Ford Motor Company, at 1827.5 cm^{-1}, $\sigma(COCl_2) = 5.7 \times 10^{-19}$ cm^2 molecule^{-1}. A reference spectrum for COBrCl was obtained by irradiating $CHBr_2Cl/Cl_2$ mixtures in 700 Torr total pressure of air. COBrCl was identified as the sole carbon-containing product by comparison with the infrared spectrum reported by Overend et al.[20] Use of absorption cross sections calculated from the spectrum given in Figure 2 of ref 20 gave COBrCl yields that were an order of magnitude larger than the $CHBr_2Cl$ loss, indicating a typographical error in the calibration of the spectrum presented by Overend et al.[20] Quantification of COBrCl in the present study was based on an assumed 100% conversion of $CHBr_2Cl$ into COBrCl, at 810.7 cm^{-1}, $\sigma(COBrCl) = 2.7 \times 10^{-18}$ cm^2 molecule^{-1}. Oxygen, nitrogen, synthetic air, Cl_2, CH_4, CD_4, CH_3F, CH_3Cl, CH_2D_2, ^{13}CO, $CHBrCl_2$, $CHBr_2Cl$, CBr_2Cl_2, and $CBrCl_3$ were obtained at the highest purities available from commercial sources. $CHBrCl_2$, CBr_2Cl_2, CH_2BrCl, CH_2Br_2 are liquids at 296 K and were degassed by several freeze−pump−thaw cycles before use. All other compounds were used as received. All uncertainties reported in this paper are two standard deviations unless otherwise stated. Standard error propagation methods are used to calculate combined uncertainties.

3. $CHBrCl_2$ and CH_2BrCl

3.1. Relative-Rate Study of Cl + $CHBrCl_2$ and Cl + CH_2BrCl.

The rate constants for the reaction of Cl atoms with $CHBrCl_2$ and CH_2BrCl were measured over the temperature range 217−296 K, relative to reactions 4 and 5 and to each other. All experiments were performed in 700 Torr total pressure of N_2, air, O_2, or air with NO added. Results were insensitive to the nature of the diluent and the presence of NO. Irradiation times were 1−40 min. Control experiments showed no loss (<2%) of $CHBrCl_2$, CH_2BrCl, or CH_2Br_2 due to photolysis or dark chemistry over the experimental time scale.

$$Cl_2 + h\nu \rightarrow 2Cl \tag{1}$$

$$Cl + CHBrCl_2 \rightarrow products \tag{2}$$

$$Cl + CH_2BrCl \rightarrow products \tag{3}$$

$$Cl + CH_4 \rightarrow CH_3 + HCl \tag{4}$$

$$Cl + CH_2Br_2 \rightarrow products \tag{5}$$

Relative-rate data obtained at 296 K are shown in Figures 1 (k_2) and 2 (k_3) and are summarized in Table 1. Using $k_4 = 1.1 \times 10^{-11} \exp(-1400/T)$ cm^3 molecule^{-1} s^{-1} [21] and $k_5 = 6.4 \times 10^{-12} \exp(-807/T)$ cm^3 molecule^{-1} s^{-1}, we derive $k_2 = (1.5 \pm 0.2) \times 10^{-13}$ and $k_3 = (4.3 \pm 0.7) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The quoted uncertainty reflects two standard deviations from the fits in Figures 1 and 2 and a 10% potential systematic error associated with uncertainties in the reference rate constants. Our result for k_3 is in good agreement with the previous determinations of $k_3 = (4.2 \pm 0.5) \times 10^{-13}$ [22] and $k_3 = (4.1 \pm 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[23] There are no previous measurements of k_2 in the literature to compare with our results.

Relative-rate studies were also performed at temperatures of 217, 229, 250, and 274 K. Each relative-rate determination was performed in N_2 and either air or O_2. Data obtained at the two temperature extremes in the study of $CHBrCl_2$ versus CH_4 are shown in Figure 3. Measured rate constant ratios are given in Table 1, and it can be seen that the measured values of k_2/k_3 are consistent with the ratios $(k_2/k_4)/(k_3/k_4)$ and $(k_2/k_5)/(k_3/k_5)$ showing the internal consistency of the data set. Absolute rate coefficients for reactions 2 and 3 were obtained using $k_4 = 1.1$

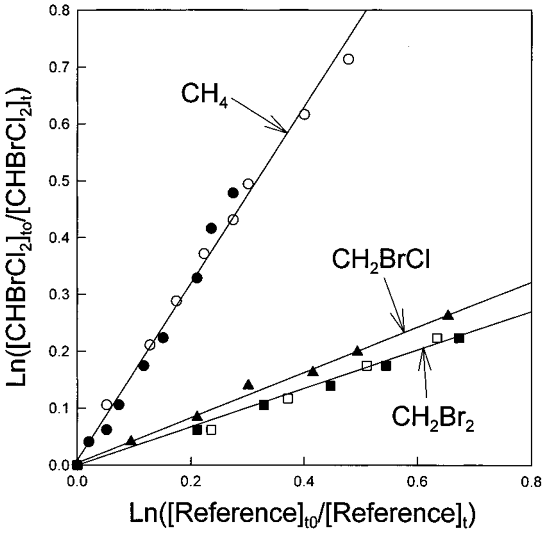

Figure 1. Loss of $CHBrCl_2$ vs CH_4 (●), CH_2BrCl (▲), or CH_2Br_2 (■) in the presence of Cl atoms in 700 Torr total pressure of either N_2 (open symbols) or air, or O_2 diluent (filled symbols); $T = 296$ K.

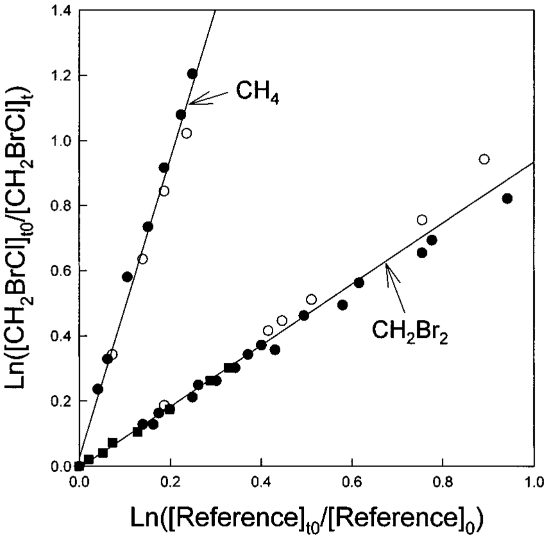

Figure 2. Loss of CH_2BrCl vs CH_4 and CH_2Br_2 in the presence of Cl atoms in 700 Torr total pressure of N_2 (○), air or O_2 (●), or air with NO added (■); $T = 296$ K.

$\times 10^{-11} \exp(-1400/T)$ [ref 21] and $k_5 = 6.4 \times 10^{-12} \exp(-807/T)$ [ref 13] cm^3 $molecule^{-1}$ s^{-1}. Table 1 also gives the absolute values for k_2 and k_3. Figure 4 shows Arrhenius plots for the reactions of Cl atoms with CH_2BrCl and $CHBrCl_2$. As seen in Figure 4, consistent results were obtained using CH_4 (open symbols) and CH_2Br_2 (filled symbols) as reference compounds. We estimate that uncertainties in the reference rate constants are ±10%. Statistical uncertainties in the measured rate-constant ratios were typically ±5%. Linear least-squares analysis of the data (using both references) in Figure 4 gives the following Arrhenius parameters: $k_2 = (2.58 \pm 0.39) \times 10^{-12} \exp(-852 \pm 76/T)$ and $k_3 = (1.20 \pm 0.18) \times 10^{-11} \exp(-1000 \pm 82/T)$ cm^3 $molecule^{-1}$ s^{-1}.

Our expression for k_3 is in fair agreement with the only previously reported temperature-dependent measurement, that of Tschuikow-Roux et al.,[23] who determined $k_3/k_4 = 3.92 \exp(28/T)$ over the range 273−368 K, from which $k_3 = 4.3 \times 10^{-11} \exp(-1370/T)$ can be obtained. The two expressions yield indistinguishable values for k_3 in the range 273−296 K, but diverging values are obtained at the temperature extremes of the combined data set. Our 217 K data point is about a factor of 2 higher than the value obtained by extrapolation of the Tschuikow-Roux et al.[23] Arrhenius expression. Extrapolation of our Arrhenius expression to 368 K yields a value that is 20% lower than that reported by Tschuikow-Roux et al.[23] A fit to the combined data set yields $k_3 = 2.1 \times 10^{-11} \exp(-1140/T)$, which agrees to within 11% with all measurements. Table 2 shows Arrhenius parameters for the reaction of Cl atoms with a series of bromo- and chloromethanes. As seen from the table and discussed in section 8, both the preexponential factor and the activation energy decrease with increasing bromine substitution.

TABLE 1: Kinetic Data for the Reactions of Cl + $CHBrCl_2$ (2) and Cl + CH_2BrCl (3)[a]

Relative Rate Data

T (K)	k_3/k_4	k_3/k_5	k_2/k_4	k_2/k_5	k_2/k_3
296	4.60	0.94	1.55	0.35	0.40
274	4.64	0.87	1.74	0.34	0.38
250	5.52	0.88	1.93	0.34	0.39
229	5.63	0.79	2.42	0.36	0.36
217	6.40	0.84	2.84	0.36	0.40

Absolute Rate Data

T (K)	$k_3 \times 10^{13}$	$k_3 \times 10^{13}$	$k_2 \times 10^{13}$	$k_2 \times 10^{13}$
296	4.47	3.94	1.51	1.47
274	3.08	2.93	1.16	1.14
250	2.25	2.23	0.79	0.86
229	1.37	1.49	0.59	0.68
217	1.11	1.30	0.49	0.56

[a] Absolute rates are calculated using $k_4 = 1.1 \times 10^{-11} \exp(-1400/T)$ [21] and $k_5 = (6.4 \pm 0.6) \times 10^{-12} \exp(-807 \pm 50/T)$ cm^3 $molecule^{-1}$ s^{-1}.[13]

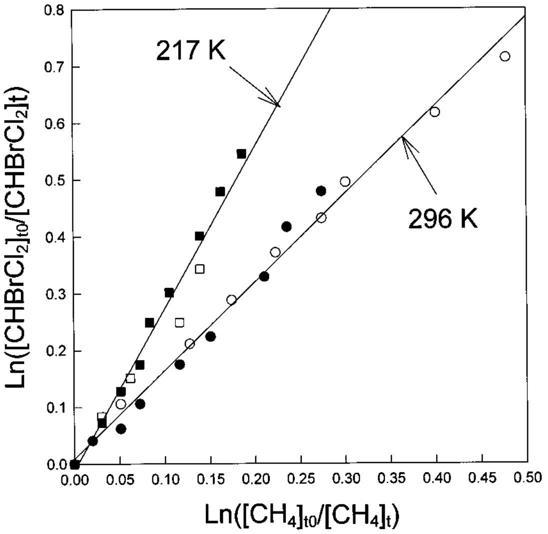

Figure 3. Loss of $CHBrCl_2$ vs CH_4 in the presence of Cl atoms in 700 Torr total pressure of either N_2 (open symbols) or air (filled symbols) at 296 K (circles) and 217 K (squares).

3.2. Kinetics of the Reactions of OH Radicals with CH_2BrCl and $CHBrCl_2$. Relative-rate experiments were performed to study the kinetics of the reactions of OH radicals with CH_2BrCl and $CHBrCl_2$ at 296 K. OH radicals were generated by photolysis of O_3 in the presence of H_2O.

$$O_3 + h\nu\ (\lambda < 315\ \text{nm}) \rightarrow O(^1D) + O_2 \qquad (6)$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad (7)$$

Molecular oxygen was added in a quantity large enough (1.8−

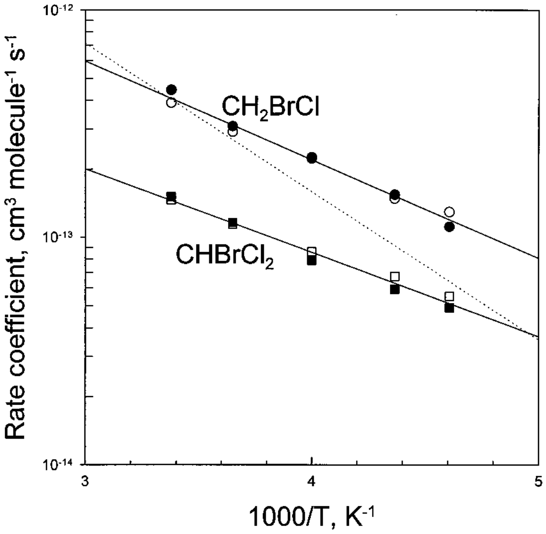

Figure 4. Arrhenius plot for reactions of Cl atoms with $CHBrCl_2$ (■) and CH_2BrCl (●). Open symbols were data measured relative to CH_4, while filled symbols were measured relative to CH_2Br_2. The dotted line shows the Arrhenius plot from Tschuikow-Roux et al.[23] for the reaction of Cl atoms with CH_2BrCl.

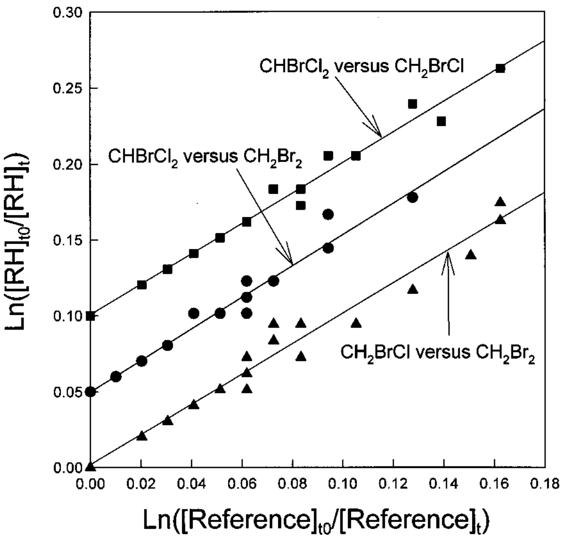

Figure 5. Plot of the decay of $CHBrCl_2$ and CH_2BrCl vs references in the presence of OH radicals in 700 Torr total pressure of helium. For clarity, data for $CHBrCl_2$ vs CH_2Br_2 and CH_2BrCl are shifted vertically by 0.05 and 0.10 units, respectively.

5.1 Torr) to scavenge any $O(^3P)$ formed in the photolysis of O_3 for wavelengths greater than 300 nm but small enough not to quench $O(^1D)$ radicals formed in reaction 6. Helium was used as the bath gas to minimize quenching of $O(^1D)$. The rate constants for reactions 8 and 9 were measured relative to both reaction 10 and to each other; the results are shown in Figure 5. Variation of the initial concentration ratios $[CH_2BrCl]_0/[CH_2Br_2]_0$ and $[CHBrCl_2]_0/[CH_2BrCl]_0$ by factors of 2 and 1.6 had no discernible influence on the rate constant ratios.

$$OH + CHBrCl_2 \rightarrow \text{products} \tag{8}$$

$$OH + CH_2BrCl \rightarrow \text{products} \tag{9}$$

$$OH + CH_2Br_2 \rightarrow \text{products} \tag{10}$$

Linear least-squares analysis of the data in Figure 5 gives $k_8/k_{10} = 1.03 \pm 0.08$, $k_8/k_9 = 1.00 \pm 0.07$, and $k_9/k_{10} = 1.00 \pm 0.08$. Using $k_{10} = (1.2 \times 0.3) \times 10^{-13}$[13] gives $k_8 = (1.2 \pm 0.3) \times 10^{-13}$ and $k_9 = (1.2 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This is, to the best of our knowledge, the first measurement of k_8, although an estimate of 9.6×10^{-14} cm^3 molecule^{-1} s^{-1} has been made[24] on the basis of the trends in the reactivity of a suite of halogenated methanes and ethanes toward OH.

TABLE 2: Arrhenius Parameters for the Reactions Cl + RH → R + HCl

RH	A (10^{11} cm^3 molecule^{-1} s^{-1})	E_a (kcal mol^{-1})	k_{296K} (10^{-13} cm^3 molecule^{-1} s^{-1})	ref
CH_4	1.1	2.8	1.0	21
CH_3Cl	3.2	2.5	4.8	21
CH_2Cl_2	3.1	2.7	3.3	21
CH_3Br	1.5	2.1	4.2	12
CH_2BrCl	1.2	2.0	4.1	this work
$CHBrCl_2$	0.26	1.7	1.5	this work
CH_2Br_2	0.64	1.6	4.2	13

Two values for k_9 have been published. Orkin et al.[25] used flash photolysis resonance fluorescence and discharge flow electron paramagnetic resonance techniques over the range 277–370 K and reported $k_9 = 3.04 \times 10^{-12} \exp(-978/T)$ giving 1.1×10^{-13} cm^3 molecule^{-1} s^{-1} at 296 K. DeMore[24] reported $k_9 = 1.8 \times 10^{-12} \exp(-906/T)$ (8.4×10^{-14} cm^3 molecule^{-1} s^{-1} at 296 K) using a relative-rate technique. The DeMore[24] value was obtained relative to reaction of OH with CH_2Cl_2, for which a value of 8.2×10^{-14} cm^3 molecule^{-1} s^{-1} was used. If the currently recommended[21] value for this reference reaction (1.1×10^{-13} cm^3 molecule^{-1} s^{-1}) is adopted, a higher value for k_9, 1.2×10^{-13} cm^3 molecule^{-1} s^{-1}, is obtained. The similarity of the rate coefficients k_8, k_9, and k_{10} is not surprising, since all reported rate coefficients for the reaction of OH with di- and trisubstituted chlorobromomethanes fall in the range $(1.0–1.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (see DeMore et al.[21]).

3.3. Product Study of the Cl-Initiated Oxidation of $CHBrCl_2$: Evidence for the “Hot Alkoxy Radical” Effect. To investigate the mechanism of the reaction of Cl atoms with $CHBrCl_2$, mixtures of 15.4–20.7 mTorr of $CHBrCl_2$ and 207–213 mTorr of Cl_2 in 700 Torr of air or O_2 diluent were irradiated. Inspection of the IR spectra given in Figure 6 shows clearly that $COCl_2$ is a major product of the oxidation. Apart from a small yield of COBrCl (1.8 ± 0.7%) no other carbon-containing products were detected. The absence of HCOCl shows that reaction of Cl atoms with $CHBrCl_2$ does not proceed via abstraction of a Br atom, since this would lead to $CHCl_2O$ radicals, which eliminate Cl atoms to form HCOCl.[14]

Figure 7A shows the formation of $COCl_2$ versus the loss of $CHBrCl_2$ in experiments where NO was absent. Linear least-squares analysis gives a $COCl_2$ yield of (99 ± 5)%, showing that in the absence of NO the Cl-initiated oxidation of $CHBrCl_2$ in air proceeds predominantly via reactions 2 and 11–13. The main fate of alkoxy radicals formed from the self-reaction of $CBrCl_2O_2^\bullet$ radicals is thus elimination of a Br atom to form $COCl_2$, while the (1.8 ± 0.7)% yield of COBrCl suggests that Cl-atom elimination is a minor loss process.

$$Cl + CHBrCl_2 \rightarrow CBrCl_2 + HCl \tag{2}$$

$$CBrCl_2 + O_2 \rightarrow CBrCl_2O_2 \tag{11}$$

$$CBrCl_2O_2 + CBrCl_2O_2 \rightarrow 2CBrCl_2O + O_2 \tag{12}$$

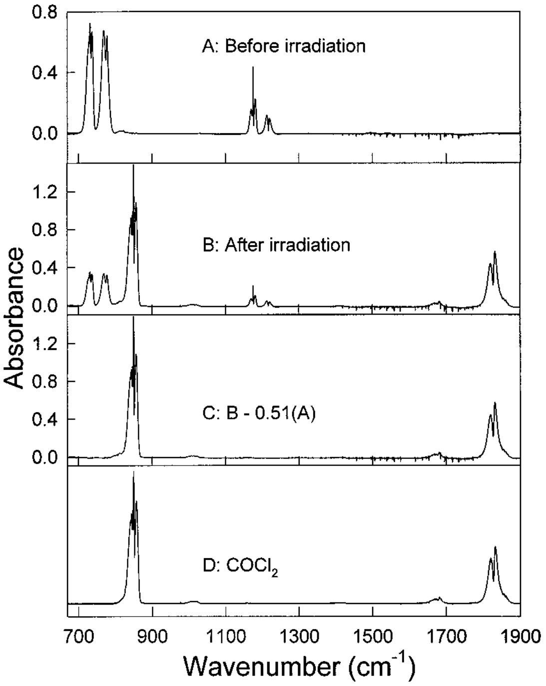

Figure 6. IR spectra taken before (A) and after (B) a 3.5-min irradiation of a mixture of 20.7 mTorr of $CHBrCl_2$ and 207 mTorr of Cl_2 in 700 Torr of air diluent. Panel C shows the product spectrum derived by subtracting 0.51 × (A) from (B). Panel D is a reference spectrum of $COCl_2$.

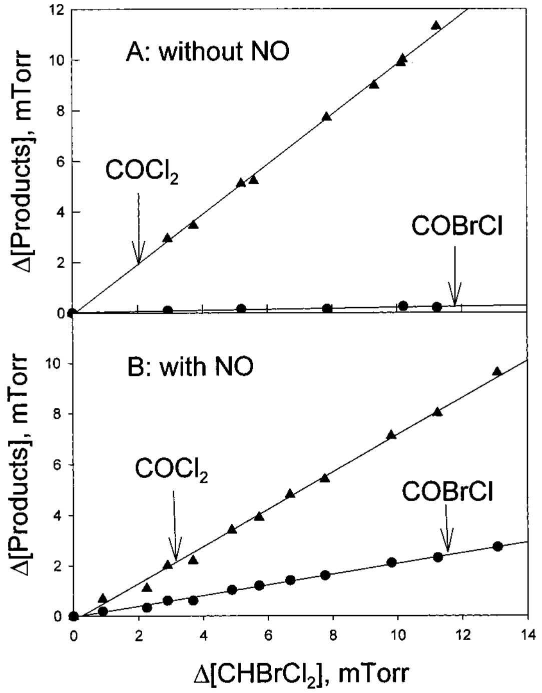

Figure 7. Formation of products vs loss of $CHBrCl_2$ following UV irradiation of mixtures of $CHBrCl_2/Cl_2$ in (A) air and (B) air with NO added.

$$CBrCl_2O \rightarrow CCl_2O + Br \tag{13}$$

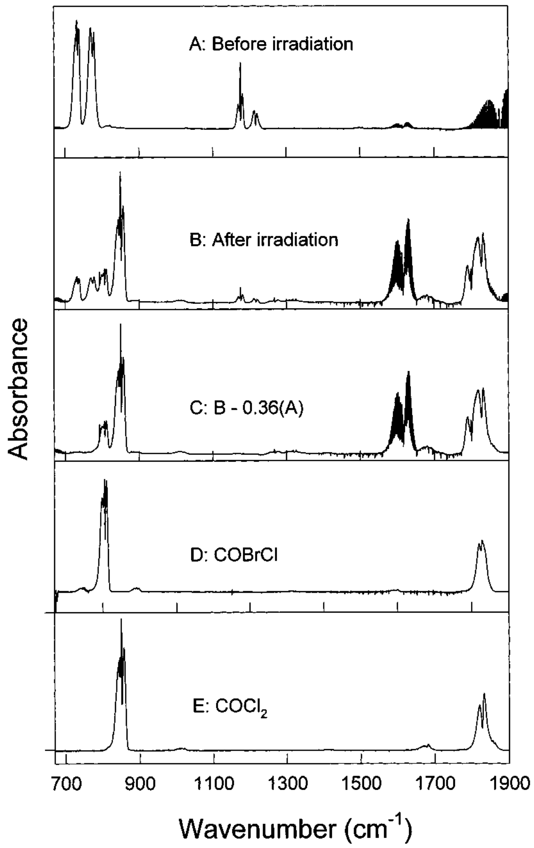

Figure 8. IR spectra taken before (A) and after (B) a 56-min irradiation of a mixture of 20.4 mTorr of $CHBrCl_2$, 224 mTorr of Cl_2, and 22.2 mTorr of NO in 700 Torr of air diluent. Panel C shows the product spectrum derived by subtracting 0.36 × (A) from (B). Panels D and E show reference spectra of COBrCl and $COCl_2$. Product features in panels A and B centered at 1617, 1799, and 1874 cm^{-1} are NO_2, ClNO, and NO, respectively.

Product studies were also conducted in 700 Torr of air with NO added. The experimental conditions were 18.1−20.4 mTorr of $CHBrCl_2$,187−224 mTorr of Cl_2, and 17.9−22.2 mTorr of NO. In the presence of NO, the peroxy radicals $CBrCl_2O_2^•$ react with NO to form $CBrCl_2O^•$ radicals (reaction 14). IR spectra taken before (Figure 8A) and after (Figure 8B) a 56-min irradiation of a mixture of 20.4 mTorr of $CHBrCl_2$, 224 mTorr of Cl_2, and 22.2 mTorr of NO in 700 Torr of air are shown in Figure 8. $COCl_2$ and COBrCl are both clearly observed as products. Figure 7B shows the yield of products versus the loss of $CHBrCl_2$. The product yields were (73 ± 4)% for $COCl_2$ and (21 ± 4)% for COBrCl. This result is significantly different from that obtained in the absence of NO. We ascribe the change in product yields when NO is present to the formation of a significant fraction of internally excited $CBrCl_2O^•$ radicals in reaction 14, which can decompose via Cl-atom elimination.

$$CBrCl_2O_2 + NO \rightarrow CBrCl_2O^* + NO_2 \tag{14}$$

$$CBrCl_2O^* \rightarrow COBrCl + Cl \tag{15}$$

Similar experiments were conducted at NCAR at 295, 273, and 253 K. Results at the three temperatures were indistinguishable from one other and from the Ford results, consistent with the occurrence of chemical activation. In the absence of NO, the major product observed in the oxidation of $CHBrCl_2$ was $COCl_2$, with a yield of (99 ± 5)%. When NO was added to the system, both $COCl_2$ (73 ± 4%) and COBrCl (21 ± 4%) were observed.

The necessary thermodynamic data for calculating heats of reactions for reactions 12 and 14 or the C−Cl and C−Br bond strengths in $CBrCl_2O$ are not available. However, it seems reasonable to assume that the C−Cl bond in the $CBrCl_2O^•$ radical is stronger than the C−Br bond. Similarly, on the basis of the thermochemical database for peroxy and alkoxy radicals, it is reasonable to assume that reaction 14 is significantly more

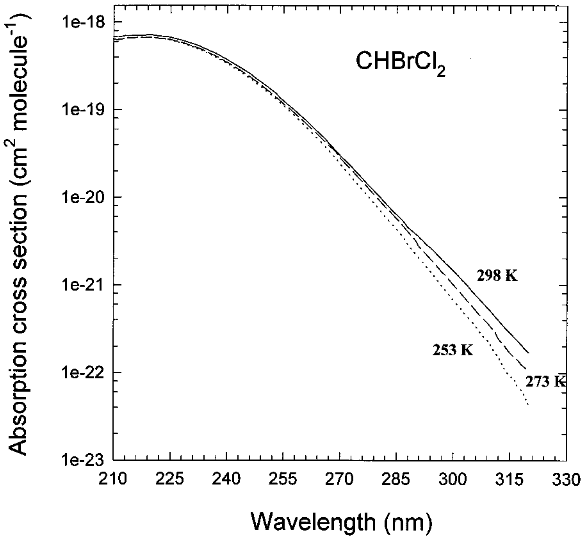

Figure 9. UV spectrum of CHBrCl$_2$ at 298, 273, and 253 K.

exothermic than reaction 12. Hence, qualitatively, the experimental observations are consistent with chemical activation of the CBrCl$_2$O$^•$ radical formed in reaction 14, making the higher-energy Cl-atom elimination channel accessible.

3.4. UV Spectrum of CHBrCl$_2$. Absorption cross sections for CHBrCl$_2$ were obtained at temperatures ranging from 253 to 298 K and over the range 210−320 nm, as shown in Figure 9. Measurements at longer wavelength were not possible, owing to the limited vapor pressure of CHBrCl$_2$. The spectrum shows a broad maximum near 220 nm. The absorption cross sections are relatively independent of temperature near the maximum but show an increasingly positive dependence on temperature at longer wavelengths.

4. CHBr$_2$Cl

4.1. Relative-Rate Study of the Reaction of Cl Atoms with CHBr$_2$Cl. Relative-rate experiments were performed to measure the rate constant for the reaction of Cl atoms with CHBr$_2$Cl. The kinetics of reaction 16 were measured relative to reactions 4 and 17−19 in 700 Torr of air, N$_2$, or O$_2$.

$$\mathrm{Cl} + \mathrm{CHBr_2Cl} \rightarrow \text{products} \tag{16}$$

$$\mathrm{Cl} + \mathrm{CH_4} \rightarrow \text{products} \tag{4}$$

$$\mathrm{Cl} + {}^{13}\mathrm{CO} \rightarrow \text{products} \tag{17}$$

$$\mathrm{Cl} + \mathrm{CH_3F} \rightarrow \text{products} \tag{18}$$

$$\mathrm{Cl} + \mathrm{CD_4} \rightarrow \mathrm{CD_3} + \mathrm{DCl} \tag{19}$$

Variation of the initial concentration ratio [CHBr$_2$Cl]$_0$/[CH$_4$]$_0$ by a factor of 3 had no discernible influence on the rate-constant ratio, nor did the nature of the diluent. Control experiments showed that photolysis and heterogeneous loss of CHBr$_2$Cl were unimportant. Measured rate-constant ratios were $k_{16}/k_4 = 2.09 \pm 0.05$, $k_{16}/k_{17} = 8.03 \pm 0.38$ (in air), $k_{16}/k_{18} = 0.73 \pm 0.03$, and $k_{16}/k_{19} = 29.5 \pm 2.40$. Using $k_4 = 1.0 \times 10^{-13}$,[21] $k_{17} = 3.0 \times 10^{-14}$ (in air),[26] $k_{18} = 3.2 \times 10^{-13}$,[27] and $k_{19} = 6.1 \times 10^{-15}$ [29] gives $k_{16} = (2.09 \pm 0.05) \times 10^{-13}$, $(2.41 \pm 0.11) \times 10^{-13}$, $(2.34 \pm 0.10) \times 10^{-13}$, and $(1.80 \pm 0.15) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. We estimate that potential systematic errors associated with uncertainties in the reference rate constants k_4, k_{17}, k_{18}, and k_{19} could add an additional 10% to the uncertainty ranges for k_{16}. Propagating this additional uncertainty gives $k_{16} = (2.09 \pm 0.21) \times 10^{-13}$, $(2.41 \pm 0.26) \times 10^{-13}$, $(2.34 \pm 0.25) \times 10^{-13}$, and $(1.80 \pm 0.23) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. We choose to cite a final value for k_{16} that is an average of the four determinations with error limits that encompass the extremes of the determinations. Hence, $k_{16} = (2.2 \pm 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K. To the best of our knowledge, this is the first measurement of k_{16}.

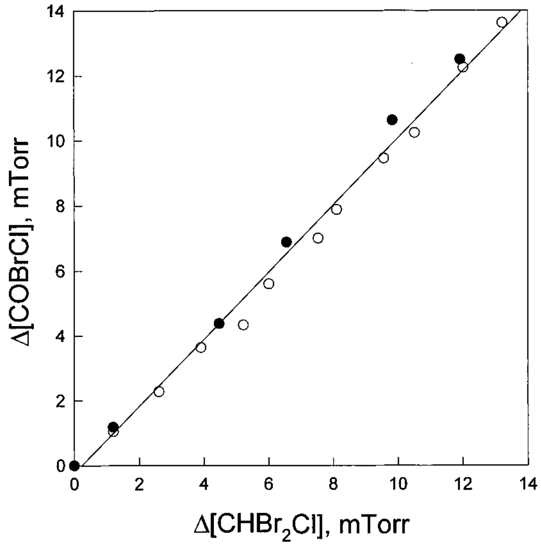

Figure 10. Formation of COBrCl vs loss of CHBr$_2$Cl in the presence of Cl atoms in 700 Torr of air (●) or air with NO added (○).

4.2. Product Study of the Cl-Initiated Oxidation of CHBr$_2$Cl. The products of the Cl-atom-initiated oxidation of CHBr$_2$Cl were studied using mixtures of 30 mTorr of CHBr$_2$Cl and 104 mTorr of Cl$_2$ in 700 Torr of air diluent, with and without 15 mTorr of added NO. Following UV irradiation, COBrCl was identified as the sole carbon-containing product in all experiments. As seen in Figure 10, the formation of COBrCl scaled linearly with the loss of CHBr$_2$Cl and the product yields were not affected by the presence of NO. Linear least-squares analysis gives a COBrCl yield of (104 ± 10)%.

The reaction of Cl atoms with CHBr$_2$Cl may proceed via hydrogen or bromine abstraction:

$$\mathrm{Cl} + \mathrm{CHBr_2Cl} \rightarrow \mathrm{CBr_2Cl} + \mathrm{HCl} \tag{16a}$$

$$\mathrm{Cl} + \mathrm{CHBr_2Cl} \rightarrow \mathrm{CHBrCl} + \mathrm{ClBr} \tag{16b}$$

Previous studies have shown that in air diluent, there is rapid and quantitative conversion of CHBrCl radicals into HC(O)Cl.[22] The absence of any observable HCOCl (<1%) shows that the reaction of Cl atoms with CHBr$_2$Cl proceeds predominantly via channel 16a. The absence of any observable COBr$_2$ shows that the fate of the alkoxy radical CBr$_2$ClO$^•$ formed via self-reaction of peroxy radicals or by reaction of the peroxy radical with NO is elimination of a bromine atom.

4.3. UV Spectrum of CHBr$_2$Cl. The UV absorption spectrum of CHBr$_2$Cl was measured at 296, 261, and 240 K, as shown in Figure 11. The long-wavelength extent of the measurements was limited by the vapor pressure of CHBr$_2$Cl (15 Torr at 298 K, 0.35 Torr at 240 K). Two absorption bands are apparent, one maximizing near 210 nm and the other near 240 nm. Near the band maxima, low-temperature cross sections are approximately 10% higher than those at room temperature. A positive temperature dependence of the cross section is evident

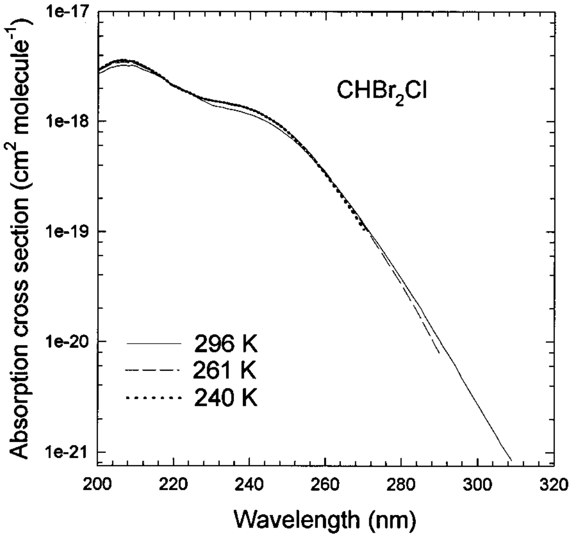

Figure 11. UV spectrum of $CHBr_2Cl$ at 296, 261, and 240 K.

in the long-wavelength tail of the spectrum. The room-temperature cross section is about 15% higher at 270 nm than that obtained at 240 K. Absorption cross sections for $CHBr_2Cl$ are higher than those of $CHBrCl_2$ over the entire wavelength region studied. The atmospheric photolysis rate of $CHBr_2Cl$, based on the spectrum reported here, is discussed in section 7.

5. CBr_2Cl_2 and $CBrCl_3$

5.1. Relative-Rate Studies of the Reactions of Cl Atoms with CBr_2Cl_2 and $CBrCl_3$.

Reaction of Cl atoms with $CBrCl_3$ via Br abstraction has been reported at high temperatures.[28] Thus, the reaction of Cl atoms with CBr_2Cl_2 was studied as a potential source of $CBrCl_2$ radicals. The reaction of Cl atoms with $CBrCl_3$, a potential product in reaction 20, was also investigated.

Relative-rate experiments were performed to measure the rate constant for the reaction of Cl atoms with CBr_2Cl_2. The kinetics of reaction 20 were measured relative to reactions 4, 21, and 22 in 700 Torr of air and to reaction 17 in 700 Torr of O_2.

$$Cl + CBr_2Cl_2 \rightarrow \text{products} \tag{20}$$

$$Cl + CH_4 \rightarrow \text{products} \tag{4}$$

$$Cl + {}^{13}CO \rightarrow \text{products} \tag{17}$$

$$Cl + CH_2D_2 \rightarrow \text{products} \tag{21}$$

$$Cl + CH_3Cl \rightarrow CH_2Cl + HCl \tag{22}$$

The observed loss of CBr_2Cl_2 versus those of CH_2D_2, CH_4, CH_3Cl, and ^{13}CO in the presence of Cl atoms is shown in Figure 12. Variation of the concentration ratios over the ranges $[CBr_2Cl_2]/[CD_2H_2] = 0.1-1$, $[CBr_2Cl_2]/[CH_4] = 0.2-2.0$, and $[CBr_2Cl_2]/[CH_3Cl] = 0.11-0.23$ had no discernible influence on the measured rate-constant ratios indicating that secondary chemistry is unimportant. Control experiments showed that loss of CBr_2Cl_2 due to photolysis and dark chemistry was unimportant.

Linear least-squares analysis of the data in Figure 12 gives $k_{20}/k_{17} = 4.71 \pm 0.25$, $k_{20}/k_{21} = 4.23 \pm 0.15$, $k_{20}/k_4 = 1.79 \pm 0.09$, and $k_{20}/k_{22} = 0.37 \pm 0.03$. Using $k_{17} = 3.4 \times 10^{-14}$ (in O_2),[26] $k_{21} = 4.6 \times 10^{-14}$,[29] $k_4 = 1.0 \times 10^{-13}$,[21] and $k_{22} = 4.9 \times 10^{-13}$ [21] gives $k_{20} = (1.60 \pm 0.08) \times 10^{-13}$, $(1.95 \pm 0.07) \times 10^{-13}$, $(1.79 \pm 0.09) \times 10^{-13}$, and $(1.81 \pm 0.15) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. Assuming that potential systematic errors associated with uncertainties in the reference rate constants could add an additional 10% to the uncertainty ranges for k_{20}, we cite a final value $k_{20} = (1.8 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, which is an average of the four determinations with error limits that encompass the extremes of the determinations. To the best of our knowledge, this is the first measurement of k_{20}.

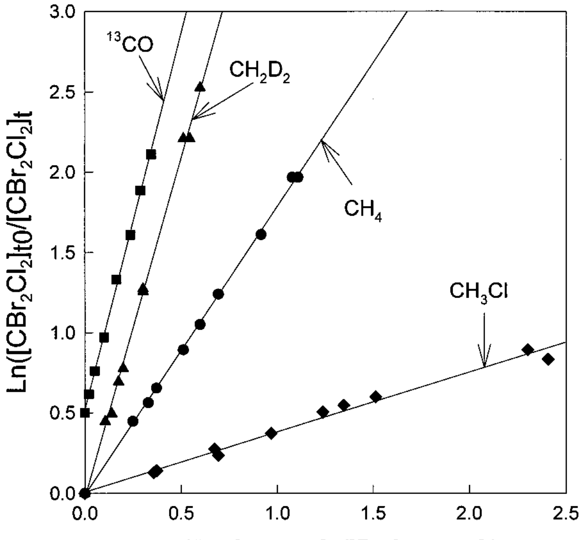

Figure 12. Loss of CBr_2Cl_2 vs ^{13}CO (■), CH_2D_2 (▲), CH_4 (●), CH_3Cl (◆) in the presence of Cl atoms in 700 Torr total pressure of air. For clarity, the data using ^{13}CO reference has been shifted vertically by 0.5 units.

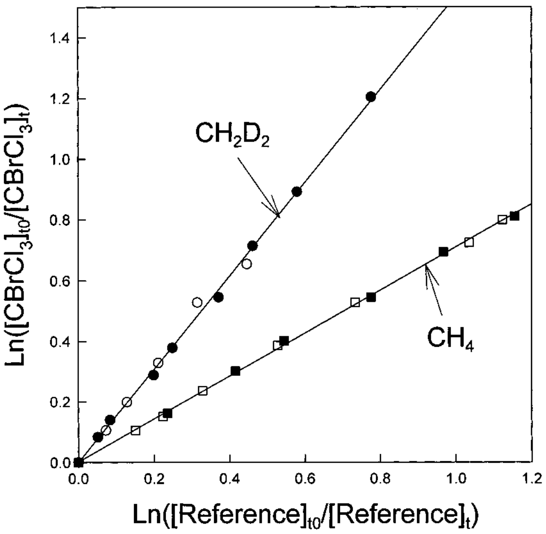

Figure 13. Loss of $CBrCl_3$ vs CH_2D_2 (●) and CH_4 (■) in the presence of Cl atoms in 700 Torr total pressure of N_2 (open symbols) or O_2 (filled symbols).

The rate constant k_{23} for the reaction of Cl atoms with $CBrCl_3$ at 296 K was measured using reactions 4 and 21 as references.

$$Cl + CBrCl_3 \rightarrow \text{products} \tag{23}$$

The observed loss of $CBrCl_3$ versus those of CH_2D_2 and CH_4 in the presence of Cl atoms is shown in Figure 13. Variation of the concentration ratios over the ranges $[CBrCl_3]/[CD_2H_2] = 0.1-0.9$ and $[CBrCl_3]/[CH_4] = 0.2-0.3$ had no discernible influence on the measured rate-constant ratios, indicating that secondary chemistry is unimportant. Experiments were per-

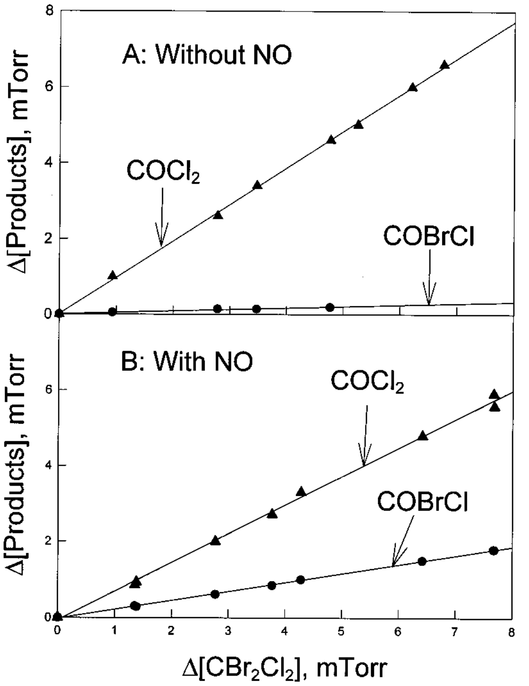

Figure 14. Formation of products vs loss of CBr_2Cl_2 following UV irradiation of mixtures of CBr_2Cl_2/Cl_2 in (A) air and (B) air with NO added.

formed in 700 Torr total pressure of N_2 (open symbols) and O_2 (filled symbols). Irradiation times were 6−15 min in total. Loss of $CBrCl_3$ due to photolysis and dark chemistry was unimportant.

Linear least-squares analysis of the data in Figure 13 gives $k_{23}/k_4 = 0.71 \pm 0.01$ and $k_{23}/k_{21} = 1.53 \pm 0.08$. Using $k_4 = 1.0 \times 10^{-13}$ [21] and $k_{21} = 4.6 \times 10^{-14}$ [29] gives $k_{23} = (7.1 \pm 0.1) \times 10^{-14}$ and $(7.0 \pm 0.5) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Potential systematic errors associated with uncertainties in the reference rate constants k_{21} and k_4 could add an additional 10% uncertainty to k_{23}. Propagating this additional uncertainty gives $k_{23} = (7.1 \pm 0.7) \times 10^{-14}$ and $(7.0 \pm 0.9) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. We choose to cite a final value for k_{23}, which is an average of the two determinations with error limits that encompass the extremes of the determinations. Hence, $k_{23} = (7.1 \pm 0.9) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K. To the best of our knowledge, this is the first measurement of k_{23}.

5.2. Mechanism of the Cl-Initiated Oxidation of CBr_2Cl_2. The aim of the experiments presented in this section was to investigate the relative importance of the possible reaction channels 20a−20c.

$$CBr_2Cl_2 + Cl \rightarrow CBrCl_2 + BrCl \qquad (20a)$$

$$CBr_2Cl_2 + Cl \rightarrow CBr_2Cl + Cl_2 \qquad (20b)$$

$$CBr_2Cl_2 + Cl \rightarrow CBrCl_3 + Br \qquad (20c)$$

CBr_2Cl_2/Cl_2 mixtures in 700 Torr total pressure of air or O_2 diluent were irradiated in the FTIR smog-chamber system with, and without, added NO. The loss of CBr_2Cl_2 and the formation of products were monitored by FTIR spectroscopy. In the first series of experiments mixtures of 9.3−10.5 mTorr of CBr_2Cl_2 and 271−282 mTorr of Cl_2 in 700 Torr of air or O_2 diluent were subject to UV irradiation. $COCl_2$ and COBrCl were the only carbon-containing products observed. There was no discernible difference between results obtained in air and pure O_2. Figure 14A shows the formation of $COCl_2$ versus the loss of CBr_2Cl_2. Linear least-squares analysis gives a yield of $COCl_2$ of (97 ± 5)%. The yield of COBrCl was (4 ± 2)%. The formation of $COCl_2$ in a yield of essentially 100% shows that channel 20b does not contribute significantly to the overall reaction. Channel 20c is exothermic by 14.5 kcal mol^{-1}. $CBrCl_3$ could react with Cl atoms via bromine abstraction to form CCl_3 radicals, and hence, $COCl_2$ could be formed either via reaction 20a or 20c. Simple model calculations using the rate constant for the loss of $CBrCl_3$ due to reaction with Cl atoms, $k_{23} = (7.1 \pm 0.9) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $k_{20} = (1.8 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, determined in section 5.1 show that if $CBrCl_3$ is formed via reaction 20c in any significant amount, it should be visible in the spectra. The absence of any observable $CBrCl_3$ shows that channel 20c is not significant.

A second series of experiments was performed using mixtures of 12.6−13.5 mTorr CBr_2Cl_2 and 237−244 mTorr Cl_2 in 700 Torr total pressure of air to which 12−14 mTorr of NO was added. After UV irradiation two carbon-containing products were observed: $COCl_2$ and COBrCl. Figure 14B shows a plot of the observed formation of $COCl_2$ and COBrCl versus the loss of CBr_2Cl_2. Linear least-squares analysis of the data in Figure 14B gives a $COCl_2$ yield of (76 ± 4)% and a COBrCl yield of (24 ± 2)%. These results are indistinguishable from those obtained from the Cl-atom-initiated oxidation of $CHBrCl_2$ described in section 3.2. We conclude that the reaction of Cl atoms with CBr_2Cl_2, reaction 20, proceeds via Br atom abstraction to give $CBrCl_2$ radicals.

The abstraction of a Br atom from a halocarbon by Cl atoms is not commonly encountered. For example, abstraction of a Br atom by Cl from CH_3Br, CF_3Br, and CH_2Br_2 is endothermic by 17−18 kcal/mol. This type of reaction appears to be unique to the species CBr_xCl_{4-x}, for which Br abstraction by Cl is calculated to be only 1−2 kcal/mol endothermic. Reaction of Cl with $CBrCl_3$ was previously investigated by Clyne and Walker[28] at elevated temperatures. They report $k_{23} = 2.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 652 K. An approximate rate coefficient of $k_{23} = 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} was reported at 300 K, in fair agreement with our value (7.1×10^{-14} cm^3 molecule^{-1} s^{-1}). If our room-temperature value is combined with the high-temperature value of Clyne and Walker, an activation energy of 1.3 kcal/mol is obtained.

6. $CF_3CHBrCl$

6.1. Rate and Mechanism of the Cl-Initiated Oxidation of $CF_3CHBrCl$ (Halothane). The rate coefficient for reaction of Cl with $CF_3CHBrCl$, k_{24}, was measured in 700 Torr of air relative to k_4, k_{25} and k_{26}.

$$Cl + CF_3CHBrCl \rightarrow CF_3CBrCl + HCl \qquad (24)$$

$$Cl + CF_3CHCl_2 \rightarrow CF_3CCl_2 + HCl \qquad (25)$$

$$Cl + CHD_3 \rightarrow CD_3 + HCl \qquad (26)$$

Initial concentrations employed were Cl_2 (350−475 mTorr), $CF_3CHBrCl$ (2.9−18 mTorr), and one of the three reference gases CH_4 (20−46 mTorr), CHD_3 (17−19 mTorr), or CF_3CHCl_2 (4.7−6.8 mTorr). The measured rate-constant ratios were $k_{24}/k_4 = 0.20 \pm 0.02$, $k_{24}/k_{25} = 1.62 \pm 0.12$, and $k_{24}/k_{26} = 0.87 \pm 0.06$. Using $k_4 = 1.0 \times 10^{-13}$,[21] $k_{25} = 1.2 \times 10^{-14}$,[21] and $k_{26} = 2.2 \times 10^{-14}$,[29] and including potential systematic errors, yields $k_{24} = (2.0 \pm 0.3) \times 10^{-14}$, $(1.9 \pm 0.2) \times 10^{-14}$, and $(1.9 \pm 0.2)10^{-14}$ cm^3 molecule^{-1} s^{-1}, respectively. Our final value for k_{24}, $(2.0 \pm 0.3) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, is obtained

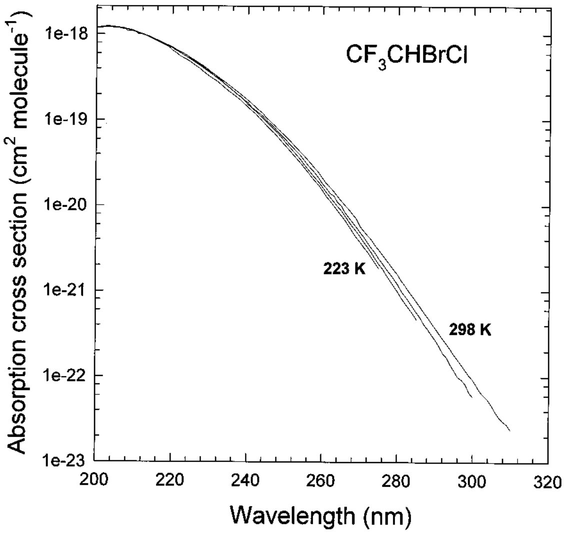

Figure 15. UV spectrum of $CF_3CHBrCl$ at 298, 273, 248, and 223 K.

from the average of these three determinations. To the best of our knowledge, this is the first measurement of k_{24}.

Products of the Cl-atom-initiated oxidation of $CF_3CHBrCl$ in 700 Torr air were determined in the absence and presence of NO. In the absence of NO, the only product observed was CF_3COCl with a yield of (93 ± 10)%, consistent with Br-atom elimination from the $CF_3CBrClO$ radical:

$$CF_3CBrCl + O_2 \rightarrow CF_3CBrClO_2 \tag{27}$$

$$2CF_3CBrClO_2 \rightarrow 2CF_3CBrClO + O_2 \tag{28}$$

$$CF_3CBrClO + M \rightarrow CF_3COCl + Br \tag{29}$$

Experiments were also performed in the presence of NO to examine the possibility that internal excitation affects the product distributions:

$$CF_3CBrClO_2 + NO \rightarrow CF_3CBrClO^* + NO_2 \tag{30}$$

Because of the small rate constant for reaction of Cl with $CF_3CHBrCl$ relative to its reaction with NO, large $CF_3CHBrCl$ concentrations had to be employed in these experiments. Thus, $CF_3CHBrCl$ consumption could not be quantified and absolute product yields could not be obtained. Nonetheless, the only product observed in these experiments was CF_3COCl, indicating that internally excited $CF_3CBrClO$ radicals produced in reaction 30 decompose almost entirely by Br-atom elimination as do their thermal counterparts produced in reaction 28. This behavior is analogous to the CHBrClO radical, for which only Br-atom elimination occurs, regardless of the method of formation[22] but differs from the $CBrCl_2O$ radical, which can undergo Cl-atom and Br-atom elimination following its production from reaction of $CBrCl_2O_2$ with NO (see sections 3.3 and 5.2).

6.2. UV Absorption Spectrum of $CF_3CHBrCl$. The absorption spectrum for $CF_3CHBrCl$ was determined in the ultraviolet at temperatures ranging from 223 to 298 K, as shown in Figure 15. At 298 K, the vapor pressure is about 200 Torr and allowed for accurate measurements to about 305 nm, while at 223 K the vapor pressure is only about 3 Torr, limiting the long-wavelength extent of the measurements to 275 nm. The halothane spectrum shows a maximum near 205 nm and decreases in roughly exponential fashion to longer wavelengths. The cross sections are nearly independent of temperature near the maximum but show an increasing positive dependence on temperature to longer wavelengths. Room-temperature absorption cross sections for $CF_3CHBrCl$ have been reported previously by Orkin and Kasimovskaya;[30] agreement between the two measurements is to within 10% between 200 and 290 nm. At longer wavelengths, the two data sets still agree to within the reported uncertainties, although our data are somewhat higher (by 20% at 300 nm and 30% at 305 nm).

7. Atmospheric Chemistry of CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, and $CF_3CHBrCl$

The atmospheric lifetime of CH_2BrCl has been discussed in detail by Orkin et al.[25] The work carried out here confirms the importance of reaction with OH in the atmospheric destruction of CH_2BrCl, with a lifetime of about 120 days. Reaction of CH_2BrCl with Cl atoms is not expected to make a significant contribution to its destruction on a global scale nor does direct photolysis contribute to the tropospheric destruction of CH_2BrCl.[25] Orkin et al.[25] have reported that loss to the oceans may occur at a rate similar to that of reaction with OH, thus limiting the overall lifetime to about 75 days. The major stable product obtained in the OH-initiated oxidation of CH_2BrCl is HCOCl, which is obtained from the decomposition of the CHBrClO radical.[22]

Reaction of $CHBrCl_2$ with OH proceeds with a rate coefficient $k_8 = (1.2 \pm 0.2) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} from which a lifetime against reaction with OH of about 120 days is obtained. Reaction of $CHBrCl_2$ with Cl atoms is not expected to be of major significance on a global scale. Photolysis rates for $CHBrCl_2$ in the lower atmosphere can be estimated from the UV spectrum obtained above and from solar-flux data.[31] It was found that significant photolysis of this species occurs in the atmosphere at wavelengths longer than the 320-nm limit of our measurements. Thus, a least-squares line was fit through the logarithm of the absorption cross sections at each temperature from 270 to 320 nm, and this line was extrapolated to 350 nm to provide an estimate of the cross sections in this wavelength region. The lifetime of $CHBrCl_2$ with respect to photolysis near the earth's surface (0−5 km) was found to be about 60 days, shorter than its lifetime against reaction with OH. This photolysis rate will of course be dependent on latitude and season. Although a thorough modeling study will be required to obtain an accurate tropospheric lifetime, an estimate of 40 days can be made from the combination of photolysis and reaction with OH. The loss of this species to the oceans is also a possibility.

The stable products obtained in the atmospheric oxidation of $CHBrCl_2$ will be dependent on the nature of the initiation step. Photolysis will probably occur by Br-atom elimination, leading (through the $CHCl_2O$ radical) to the formation of HCOCl,[14] while reaction with OH or Cl will lead to formation of $COCl_2$ and COClBr as outlined above.

The atmospheric behavior of $CHBr_2Cl$ will resemble that of $CHBrCl_2$. The rate constant for its reaction with OH is likely to be very similar to that for $CHBrCl_2$ and $CHBr_3$.[24] The UV absorption spectrum of $CHBr_2Cl$ (extrapolated to long wavelengths as for $CHBrCl_2$ above), coupled with solar-flux data, yields an approximate lifetime of 50 days against photolysis, somewhat shorter than its lifetime against OH reaction (about 120 days). A combined lifetime of about 35 days is obtained.

As discussed previously,[7,8,25,32] the atmospheric lifetime of $CF_3CHBrCl$ is controlled predominantly by its reaction with OH (about 1.2 years[32]). Our measurements of the UV absorption spectrum of this compound confirm that photolysis is a

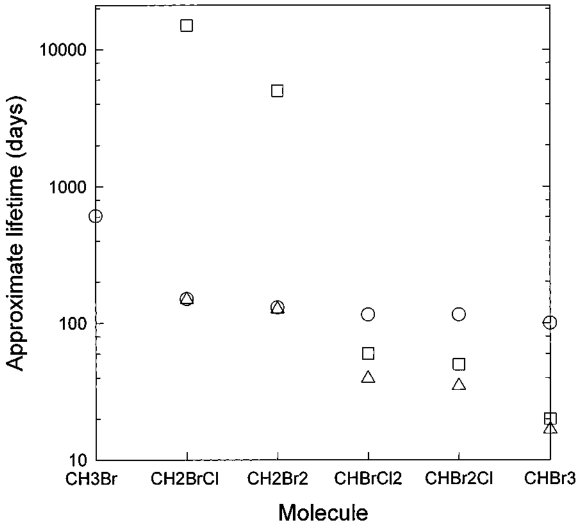

Figure 16. Approximate atmospheric lifetimes for a series of brominated methanes with respect to reaction with OH (○), photolysis (□), and both processes (△). OH rate-constant data are from ref 21 and this work. UV-photolysis rates are obtained from refs 25 (CH_2BrCl), 33, 34 ($CHBr_3$), and this work ($CHBrCl_2$ and $CHBr_2Cl$).

minor, but not insignificant, destruction pathway for halothane in the troposphere, with a lifetime of about 5−10 years.

Sufficient data are now available from which trends in the relative importance of reaction with OH and photolysis for a series of bromomethanes and bromochloromethanes can be evaluated (see Figure 16). Other than methyl bromide, the rate coefficient for reaction of OH with the series of compounds considered in Figure 16 is roughly constant ($k \approx (1-1.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}), and lifetimes versus OH reaction of about 100−150 days can be estimated. Increasing halogen (and particularly bromine) substitution leads to red shifts in the UV spectra and, hence, to increasingly rapid tropospheric photolysis rates. Photolysis is an important tropospheric loss process for the trisubstituted species $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$.[33]

8. Conclusion

The oxidation rate and mechanisms for a number of brominated organic species of interest in atmospheric chemistry have been determined. Rate constants for reaction of OH with CH_2BrCl and $CHBrCl_2$ are both 1.2×10^{-13} cm^3 molecule^{-1} s^{-1} and are important removal processes for these species. UV absorption spectra presented here show that photolysis is a major removal process for the trisubstituted methanes ($CHBrCl_2$ and $CHBr_2Cl$). Halothane, $CF_3CHBrCl$, has a somewhat longer atmospheric lifetime, and removal of this species from the atmosphere involves both reaction with OH and, to a lesser extent, photolysis.

Rate coefficients for reaction of Cl atoms with CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, and $CF_3CHBrCl$ have been determined. Rate constants for reaction of Cl atoms with mono- and disubstituted bromochloromethanes at 298 K all fall in the range $(3-5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, while reaction with trisubstituted species is somewhat slower, $(1-2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Substitution of a bromine atom for a chlorine atom within a given series (i.e., from CH_3Cl to CH_3Br, from CH_2Cl_2 to CH_2BrCl to CH_2Br_2) results in a lowering of the activation energy for the chlorine atom reaction, with a concurrent lowering of the *A* factor. The lowering of the *A* factor is likely related to steric hindrance of the larger Br atom. The presence of the CF_3 group in halothane leads to a substantially slower reaction with Cl atoms relative to the bromochloromethanes.

The behavior of the alkoxy radicals produced in the atmospheric oxidation of these species has also been studied. The alkoxy radicals $CHBrClO^{\bullet}$ and $CF_3CBrClO^{\bullet}$ react only via Br-atom elimination, regardless of whether they are formed from the peroxy radical self-reaction or via reaction of the peroxy radical with NO. In contrast, the fate of $CBrCl_2O^{\bullet}$ radicals is dependent on their mode of formation. $CBrCl_2O^{\bullet}$ radicals formed via the self-reaction of $CBrCl_2O_2^{\bullet}$ undergo Br-atom elimination to give $COCl_2$, whereas $CBrCl_2O^{\bullet}$ radicals formed by reaction of $CBrCl_2O_2^{\bullet}$ radicals with NO undergo Br- and Cl-atom elimination to give $COCl_2$ and COBrCl. This observation can be rationalized when the different exothermicities of the reactions producing the alkoxy radical $CBrCl_2O^{\bullet}$ are taken into account. Peroxy radical self-reactions are essentially thermoneutral, while the reaction of peroxy radicals with NO are exothermic by approximately 17 kcal mol^{-1}.[21] $CBrCl_2O^{\bullet}$ radicals formed in the self-reaction of $CBrCl_2O_2^{\bullet}$ radicals will possess little, or no, excitation. In contrast, a significant fraction of the $CBrCl_2O^{\bullet}$ radicals produced by the $CBrCl_2O_2^{\bullet} + NO$ reaction may possess considerable internal excitation, and additional decomposition pathways (such as elimination of a Cl atom) may be accessible for these excited radicals. Evidence for such a "hot alkoxy radical" effect has also been reported in studies of the atmospheric chemistry of HFC-134a (CF_3CFH_2) and HFC-236cb ($CF_3CF_2CFH_2$).[10,11]

Finally, a novel Br-abstraction mechanism has been shown to exist in the reaction of Cl atoms with CBr_2Cl_2 and $CBrCl_3$. The endothermicities of these reactions are about 1−2 kcal/mol. In contrast, Br-atom abstraction by Cl from other species (CH_3Br, CH_2Br_2, $CHBr_3$, $CF_3CHBrCl$) are highly endothermic (17−18 kcal/mol) and do not occur.

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