Atmospheric Chemistry of CH_2Br_2: Rate Coefficients for Its Reaction with Cl Atoms and OH and the Chemistry of the $CHBr_2O$ Radical

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ABSTRACT

Rate coefficients for the reaction of OH radicals and Cl atoms with dibromomethane, $OH + CH_2Br_2 \rightarrow CHBr_2 + H_2O$ (1) and $Cl + CH_2Br_2 \rightarrow CHBr_2 + HCl$ (3), and for the reaction of Cl atoms with methyl bromide, $Cl + CH_3Br \rightarrow HCl + CH_2Br$ (4), have been obtained using relative rate techniques. At 298 K, the value of k_1 was determined to be $(1.2 \pm 0.3) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}. The rate coefficients k_3 and k_4 were determined at a series of temperatures ranging from 228 K to 296 K and combined with the measurements of Gierczak et al., yielding the following Arrhenius expressions for k_3 and k_4; $k_3 = (6.35 \pm 0.6) \times 10^{-12} \exp(-807 \pm 50/T)$ cm^3 $molec^{-1}$ s^{-1} and $k_4 = (1.49 \pm 0.2) \times 10^{-11} \exp(-1056 \pm 50/T)$ cm^3 $molec^{-1}$ s^{-1}.

In addition, the Cl atom initiated oxidation mechanism of CH_2Br_2 in air has been studied at 298 K. The products observed were HC(O)Br and small amounts of CO. The dominant atmospheric fate of the alkoxy radical, $CHBr_2O$, is elimination of a Br atom, which occurs at a rate estimated to be greater than 4×10^6 s^{-1} in 700 torr of O_2 at 298 K. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Catalytic cycles involving reactive bromine species are important in controlling ozone concentrations in various locations in the earth's atmosphere, particu-

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larly in the lower stratosphere [1–4] and in the northern latitude marine boundary layer at polar sunrise [5–8].

Methyl bromide (CH_3Br) is an important source of bromine to the atmosphere, and has both natural and anthropogenic sources [9–11]. Dibromomethane, CH_2Br_2, is also a significant source of bromine to the atmosphere [12]. Destruction of both these gases in the atmosphere occurs mainly via reaction with OH,

$$OH + CH_2Br_2 \longrightarrow CHBr_2 + H_2O \qquad (1)$$

$$OH + CH_3Br \longrightarrow CH_2Br + H_2O \qquad (2)$$

Numerous groups [13–18] have studied the kinetics of reaction (2), and a rate coefficient $k_2 = 4.0 \times 10^{-12} \exp(-1470/T)$ is currently recommended [19]. Measurements of the rate coefficient for reaction (1) have only been published by Mellouki et al. [16] who obtained $k_1 = 1.9 \times 10^{-12} \exp(-840/T)$.

It is possible that elevated levels of Cl atoms exist in the marine boundary layer [20], particularly following polar sunrise [8]. Since rate coefficients for hydrogen abstraction by Cl atoms are in general larger than the analogous hydrogen abstraction by OH, destruction of organic compounds by Cl atoms could be of some atmospheric importance:

$$Cl + CH_2Br_2 \longrightarrow CHBr_2 + HCl \qquad (3)$$

$$Cl + CH_3Br \longrightarrow CH_2Br + HCl \qquad (4)$$

Also, laboratory studies aimed at elucidating oxidation mechanisms for atmospheric source gases are often conducted using Cl atoms to initiate the photochemistry [21] and a sound data base for reactions of Cl atoms with organic species is needed for interpretation of these experiments.

Two previous studies have been conducted of the rate coefficients for reactions (3) and (4). Tschuikow-Roux et al. [22] used a relative rate technique for determining these rate coefficients, using the reaction of Cl atoms with methane as the standard. Gierczak et al. [23] measured these rate coefficients using a direct technique, flash photolysis combined with time-resolved resonance fluorescence detection of Cl atoms. The agreement between the two studies is not good. The room temperature value of k_4 reported by Tschuikow-Roux et al. is 30% higher than that obtained by Gierczak et al., though the activation energies reported in the two studies are similar. Data for reaction of Cl atoms with CH_2Br_2 are in poorer agreement; the room temperature value of Tschuikow-Roux et al. is about 30% higher than that of Gierczak et al. and the activation energies differ by about 1.4 kcal/mole.

In this study, the rate coefficient for reaction of OH with CH_2Br_2, k_1, has been obtained at 298 K. In addition, rate coefficients for reaction of Cl atoms with CH_2Br_2 and CH_3Br, k_3 and k_4, were obtained between 228 and 296 K to resolve the discrepancies between the two previous [22,23] investigations. Finally, the mechanism of the Cl atom initiated oxidation of CH_2Br_2 has been studied under conditions of relevance to the lower atmosphere.

EXPERIMENTAL

The NCAR environmental chamber used for the determination of the relative rate coefficients has been described previously [24,25]. Briefly, the system consists of a stainless steel chamber interfaced to a Fourier Transform Spectrometer (BOMEM DA3.01) operating in the infrared. The cell is 2 m in length, with a volume of 47 l, and its temperature was controlled by flowing ethanol from a circulating bath (NESLAB ULT80-DD) through a jacket surrounding the cell. Hanst-type multi-pass optics provided a total infrared analysis pathlength of 32 m. The infrared light source was a heated ceramic coil, the beamsplitter was KBr, and the detector HgCdTe. Absorption spectra were obtained at 1 cm^{-1} resolution from the coaddition of 100–250 interferograms. Gases were added to the cell from calibrated volumes.

Relative rate coefficient measurements involving OH radicals were conducted from the photolysis of mixtures of O_3 (20–70 mtorr), O_2 (UHP Grade, U.S. Welding, 0.4–1.4 torr), H_2O ($\approx$3 torr), CH_2Br_2 (Pfaltz and Bauer, 10–16 mtorr), acetone (EM Science, 99.5% +, 10–20 mtorr), and He (UHP, U.S. Welding, 650–750 torr) at 298 K. Ozone was produced from the action of a corona discharge through O_2; this produced mixtures of about 4% O_3 in O_2, which were collected in a 1 liter bulb. Photolysis was conducted using the output of a Xe-arc lamp, filtered with a Corning 7–54 filter (240–395 nm). CH_2Br_2 and acetone were monitored using their characteristic absorptions near 1200 cm^{-1}. Direct photolysis of CH_2Br_2 and acetone in the absence of Cl_2 was not significant.

Chlorine-atom relative rate studies were conducted by photolyzing Cl_2 (Linde, HP Grade, 0.2–0.5 torr) in the presence of two of the following gases: CH_3Br (Linde, 16–60 mtorr), CH_2Br_2 (9–27 mtorr), and CH_4 (Linde, Research Grade, 8–35 mtorr). The total pressure was nominally 700 torr, and was made up with either N_2 (boil-off from a liquid N_2 dewar) or O_2. CH_2Br_2, CH_3Br, and CH_4 were monitored near 1200 cm^{-1}, between 1280–1500 cm^{-1}, and near 1300 cm^{-1}, respectively. Studies were conducted at temperatures ranging from 228 to 298 K; the temperature was constant to within ± 1 K (as determined by eight thermocouple gauges placed along the length of the cell). The photolysis source was a Xe-arc lamp, equipped with a Corning 7–51 filter to provide radiation between 340 and 400 nm. Experiments conducted in the absence of Cl_2 showed that CH_2Br_2, CH_3Br, and CH_4 were not directly photolyzed by the lamp.

The FTIR system at Ford Motor Company was interfaced to a 140 liter pyrex reactor as described previously [26]. Radicals were generated by the UV irradiation of mixtures of 0.015–2.00 torr of CH_2Br_2, 0.1–0.2 torr Cl_2, and 7–700 torr of O_2 in 700 torr total pressure with N_2 diluent at 296 K using 22 blacklamps. For relative rate determinations of k_3, CH_4 (7–13 mtorr), or CH_3Cl (33–47 mtorr) were added as reference compounds. The loss of reactants and the formation of products were monitored by FTIR spectroscopy, using an analyzing path-length of 27 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 coadded spectra. CH_2Br_2, CH_3OCH_3, CO, and HC(O)Br were monitored using their characteristic features over the wavenumber ranges 800–1600, 1080–1200, 2050–2250, and 1750–1820 cm^{-1}, respectively. With the exception of HC(O)Br, reference spectra were acquired by expanding known volumes of reference materials into the reactor. The reference spectrum of HC(O)Br was taken from the IR reference library at Ford Motor Company. Ultra pure oxygen, nitrogen, synthetic air, chlorine, and dibromomethane (>99%) were supplied by Matheson Gas Products and Aldrich Chemical Co. and used without purification.

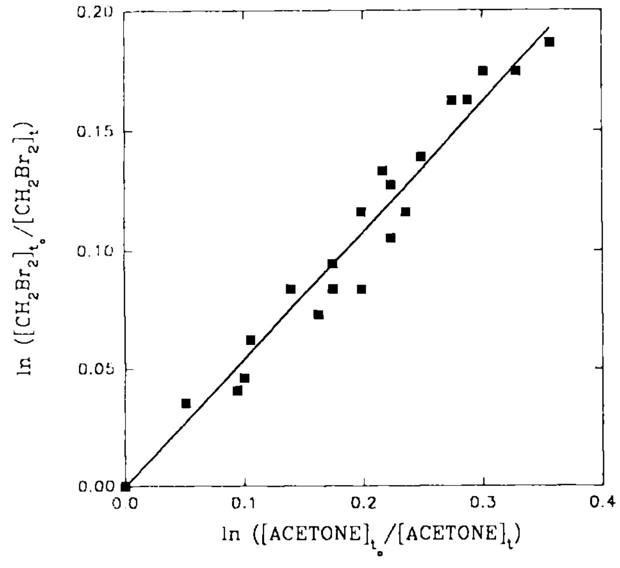

Figure 1 Plot of the decay of CH_2Br_2 versus acetone in the presence of OH at 298 K, 700 torr total pressure.

Relative rate coefficients were determined at both NCAR and Ford from the rate of disappearance of the compound under study (A) relative to that of the standard (B):

$$\ln([A]_{t_0}/[A]_t) = \frac{k_A}{k_B}\ln([B]_{t_0}/[B]_t)$$

where $[A]$ and $[B]$ are concentrations, and k_A and k_B are the rate constants for reaction of OH or Cl atoms with A and B. Relative rate constants were obtained from linear least-squares determination of the slope of plots of $\ln\{[A]_{t_0}/[A]_t\}$ vs. $\ln\{[B]_{t_0}/[B]_t\}$.

RESULTS AND DISCUSSION

Measurement of k_1

The rate coefficient for reaction (1) at 298 K was determined at NCAR relative to the rate coefficient for reaction (5),

$$OH + CH_3C(O)CH_3 \longrightarrow CH_3C(O)CH_2 + H_2O. \quad (5)$$

Photolysis of O_3 in the presence of H_2O was used as the OH source,

$$O_3 + h\nu \longrightarrow O(^1D) + O_2 \quad (6)$$

$$O(^1D) + H_2O \longrightarrow OH + OH. \quad (7)$$

Oxygen (≈ 1–3 torr) was added to the cell in sufficient quantities to scavenge $O(^3P)$ produced in the photolysis of O_3 at wavelengths longer than 300 nm, but in small enough quantities not to compete with H_2O for the $O(^1D)$. Helium was used as the buffer gas to avoid quenching $O(^1D)$. Relative rate coefficient determinations were made from four separate fills of the cell, and at least four irradiations were conducted per fill. Variation of the initial ratio of acetone to dibromomethane from 1 to 2.5 showed no systematic change in the relative rate coefficient, suggesting the lack of any complicating secondary reactions. The data obtained are shown in Figure 1 and yield a rate coefficient ratio k_1/k_5 of 0.54 ± 0.03 (95% confidence). Three determinations [27–29] of

k_5 have yielded values of (2.16 ± 0.16), (2.3 ± 0.3), and (2.7 ± 0.8) × 10^{-13} cm^3 molec^{-1} s^{-1}, respectively, from which a recommended value of k_5 = (2.3 ± 0.5) × 10^{-13} cm^3 molec^{-1} s^{-1} can be obtained [30]. Combining our k_1/k_5 ratio with this value for k_5 yields k_1 = (1.2 ± 0.3) × 10^{-13} cm^3 molec^{-1} s^{-1}, where the quoted uncertainty includes the sum of the uncertainties in the rate coefficient ratio determination and in the value of k_5. The k_1 value obtained in this work is in agreement with the previously published determination of k_1 [16], which yielded a 298 K value for k_1 of (1.13 ± 0.11) × 10^{-13} cm^3 molec^{-1} s^{-1}. In addition, a recent study [31] yielded k_1 = 1.85 × 10^{-12} exp(−836/T) cm^3 molec^{-1} s^{-1} with k_1 = 1.1 × 10^{-13} cm^3 molec^{-1} s^{-1} at 298 K, also in agreement with our value. Reaction with OH is expected to be the dominant loss for CH_2Br_2 in the atmosphere and hence its short lifetime, ≈0.4 years [16], is confirmed.

Measurement of k_3 and k_4

Relative rate determinations of the kinetics of reaction (3) were conducted at both Ford and NCAR. At Ford, k_3 was measured relative to reactions (8) and (9) in 700 torr of N_2 diluent at 296 K. The techniques used are described in detail elsewhere [32].

$$Cl + CH_4 \longrightarrow CH_3 + HCl, \qquad (8)$$

$$Cl + CH_3Cl \longrightarrow CH_2Cl + HCl \qquad (9)$$

The observed loss of CH_2Br_2 vs. those of CH_4 and CH_3Cl in 700 torr of N_2 is shown in Figure 2. Variation of the initial concentration ratios over the ranges $[CH_2Br_2]/[CH_4]$ = 1.2–3.3 and $[CH_2Br_2]/[CH_3Cl]$ = 0.3–1.0 had no discernible effect on the measured rate constant ratios suggesting the absence of complicating secondary reactions. Linear least-squares fits of the data in Figure 2 give k_3/k_8 = 4.3 ± 0.3 and k_3/k_9 = 0.94 ± 0.08. Quoted uncertainties are two standard deviations. Using recommended values [19] for k_8 = (1.0 ± 0.1) × 10^{-13} and k_9 = (4.9 ± 1.0) × 10^{-13} cm^3 molecule^{-1} s^{-1} gives k_3 = (4.3 ± 0.7) × 10^{-13} and (4.6 ± 1.3) × 10^{-13} cm^3 molecule^{-1} s^{-1} at 296 K.

At NCAR, rate coefficients for reaction (3) were determined relative to reaction (8) at temperatures of 231, 241, 254, 272, and 295 K in 700 torr of O_2 diluent. Each relative rate determination consisted of at least two fills of the cell, and at least five irradiations were conducted per fill. The initial $[CH_2Br_2]/[CH_4]$ ratio was varied by at least a factor of two at each temperature, and no systematic deviations in the relative rates were observed. Data obtained at the two temperature extremes are shown in Figure 3, and all relative rate coefficients determined are listed in Table I. Absolute rate coefficients for reaction (3) were obtained using the currently recommended [19] Arrhenius parameters for reaction (8), k_8 = 1.1 × 10^{-11} exp(−1400/T), and are also given in Table I. The uncertainty in the values of k_3 is estimated to be ± 15%, the sum of the uncertainty in the rate coefficient ratio determination (typically ±5%) and in the absolute value of k_8 (± 10%).

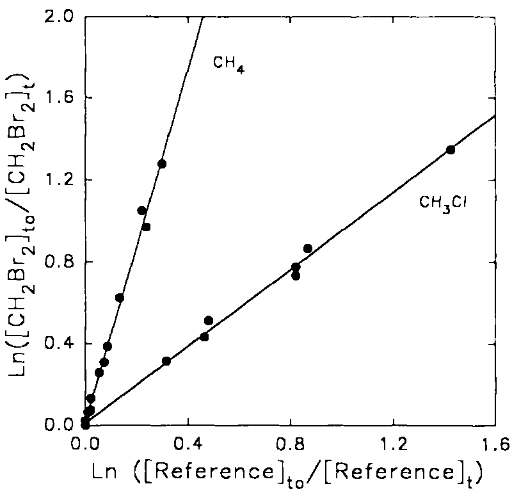

Figure 2 Plots of the decay of CH_2Br_2 versus CH_4 and CH_3Cl in the presence of Cl atoms at 296 K in 700 torr total pressure of N_2 diluent.

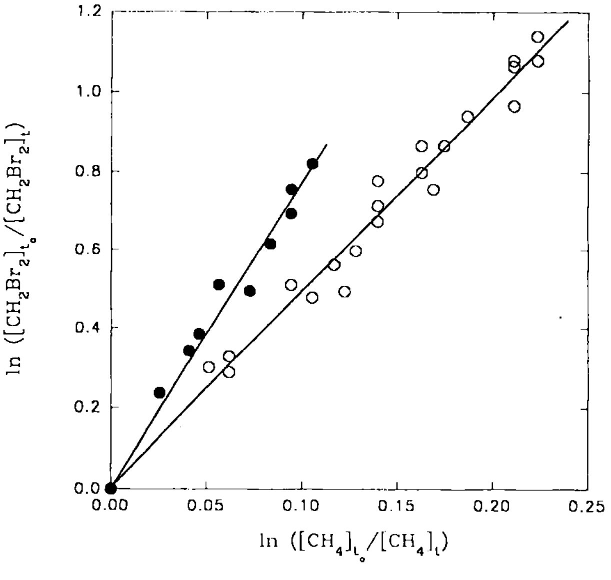

Figure 3 Plots of the decay of CH_2Br_2 versus CH_4 in the presence of Cl atoms at 700 torr O_2 pressure. ● - 231 K; ○ - 295 K.

Table I Measurements of the Rate Coefficients for Reaction of Cl Atoms with CH_2Br_2 and CH_3Br

Temp. (K)	k_3/k_8 (measured)	k_3/k_9 (measured)	k_3 (cm^3 $molec^{-1}$ s^{-1})	k_4/k_8 (measured)	k_4 (cm^3 $molec^{-1}$ s^{-1})	k_3/k_4 (measured)	k_3/k_4 (from fit)
231	7.73		1.98×10^{-13}				
241	6.6		2.18×10^{-13}				
254	6.11		2.71×10^{-13}				
272	5.57		3.56×10^{-13}				
295	4.91		4.69×10^{-13}				
296[a]	4.3		4.3×10^{-13}				
296[a]		0.94	4.6×10^{-13}				
231				6.15	1.58×10^{-13}		
244				5.64	2.00×10^{-13}		
257				5.2	2.46×10^{-13}		
278				4.83	3.45×10^{-13}		
295				4.62	4.42×10^{-13}		
228						1.24	1.27
254						1.16	1.14
272						1.17	1.06
291						1.06	1.00

[a] Data obtained at Ford. All other data from NCAR.

Rate coefficients for reaction (4) were also obtained relative to k_8, at temperatures of 231, 244, 257, 278, and 295 K. Experiments were conducted in a manner analogous to those conducted to determine k_3, except that N_2 was used as the diluent gas. Sample data at the lowest and highest temperatures are shown in Figure 4 and Table I gives the measured values of k_4/k_8 and the absolute values for k_4 at all temperatures studied. Uncertainties in the values of k_4 are again estimated to be ± 15%.

Previous determinations of k_3 and k_4 have been made by Gierczak et al. [23] (using flash photolysis-resonance fluorescence) and Tschuikow-Roux et al. [22] (using a relative rate technique with reaction (8) as the reference). These previous data for k_3 and k_4 are compared with our measurements in Figures 5 and 6, respectively. It is clear that the data obtained here for both k_3 and k_4 are in excellent agreement with the values of Gierczak et al. [23]. Indeed, there is no more than a 10% difference between any of the values obtained here for k_3 or k_4 and those obtained from the Arrhenius expressions reported by Gierczak et al. Fitting only our data, the following Arrhenius expressions are obtained: $k_3 = (9.7 \pm 1.5) \times 10^{-12} \exp(-906 \pm 80/T)$ and $k_4 = (1.78 \pm 0.25) \times 10^{-11} \exp(-1095 \pm 60/T)$. Fitting the two combined data sets yields $k_3 = (6.35 \pm 0.6) \times 10^{-12} \exp(-807 \pm 50/T)$ cm^3 $molec^{-1}$ s^{-1} and $k_4 = (1.49 \pm 0.2) \times 10^{-11} \exp(-1056 \pm 50/T)$ cm^3 $molec^{-1}$ s^{-1}. These latter values are essentially identical to the parameters originally reported by Gierczak et al. [23], and to those recommended by the NASA Panel for Data Evaluation [19].

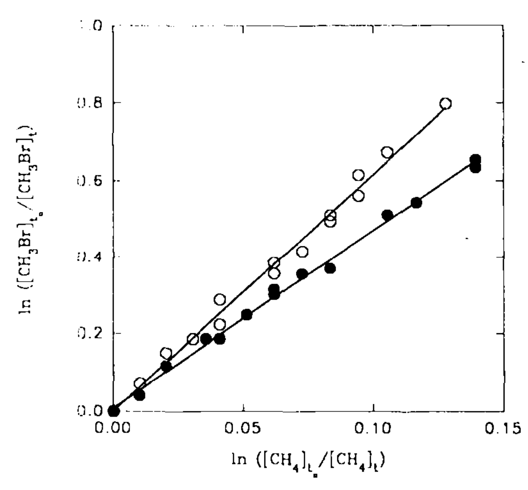

Figure 4 Plots of the decay of CH_3Br versus CH_4 in the presence of Cl atoms at 700 torr N_2 pressure. ● - 295 K; ○ - 231 K.

There is, however, substantial disagreement between our values (and those of Gierczak et al.) and the Tschuikow-Roux et al. [22] data for k_3 and k_4. As discussed by Gierczak et al., room temperature values reported by Tschuikow-Roux et al. for k_3 and k_4 are some 30% higher than those obtained here. The activation energy for k_4 reported by Tschuikow-Roux et al. is similar to that obtained here, but their activation energy for k_3 is approximately 1.4 kcal/mole higher than our value.

Although there is no obvious reason for these dis-

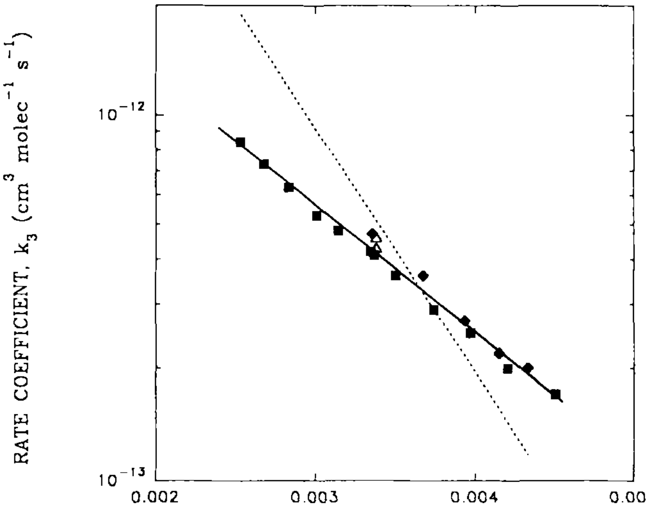

Figure 5 Arrhenius plot for reaction of Cl atoms with CH_2Br_2. ■ - Gierczak et al.[23]. ◆ - this work, NCAR. Δ - this work, Ford. Solid line - Arrhenius fit to Gierczak et al. data and data obtained in this work. Dotted line - Arrhenius parameters from Tschuikow-Roux et al.[22]

crepancies, the excellent agreement between the direct measurements of Gierczak et al. and the relative measurements made here (which are similar in methodology to those made by Tschuikow–Roux et al.) provides confidence in their validity. As a final check on the values determined for k_3 and k_4, measurements of k_3 relative to k_4 were made at 228, 254, 272, and 291 K. Ratios of k_3/k_4 obtained are shown in Table I, along with ratios obtained from the Arrhenius expressions presented above. Agreement between measured and calculated values of the k_3/k_4 ratio is excellent, with differences of less than 10% at all temperatures studied. However, it is interesting to note that the room temperature value of the k_3/k_4 ratio is slightly higher than unity, while the Arrhenius expressions predict the opposite to be true. The room temperature value for k_3 obtained relative to k_8 is also somewhat higher than the absolute room temperature

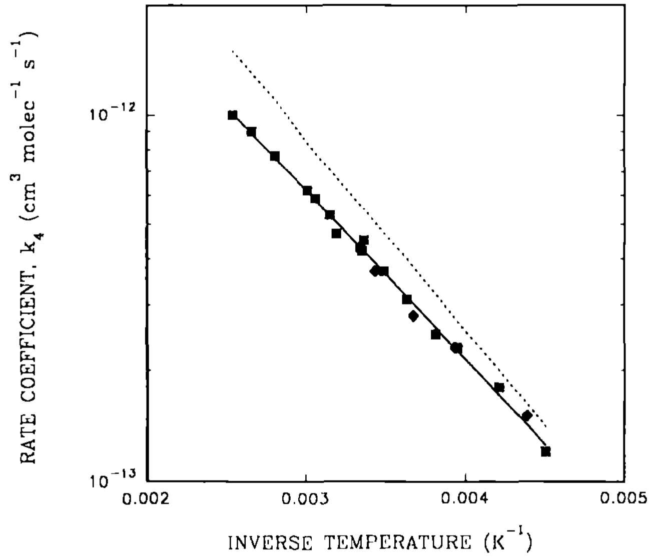

Figure 6 Arrhenius plot for reaction of Cl atoms with CH_3Br. ■ - Gierczak et al.[23]. ◆ - this work, NCAR. Solid line - Arrhenius fit to Gierczak et al. data and data obtained in this work. Dotted line - Arrhenius parameters from Tschuikow-Roux et al.[22]

value of Gierczak et al. and suggests that k_3 at room temperature may be slightly higher than the value obtained from the fit (4.5×10^{-13} cm^3 molec^{-1} s^{-1}, as opposed to 4.2×10^{-13} cm^3 molec^{-1} s^{-1}).

Study of the Atmospheric Fate of $CHBr_2O$ Radicals

The oxidation of CH_2Br_2 in the atmosphere leads to the production of $CHBr_2O$ radicals:

$$OH + CH_2Br_2 \longrightarrow CHBr_2 + H_2O \quad (1)$$

$$CHBr_2 + O_2 + M \longrightarrow CHBr_2O_2 + M \quad (10)$$

$$CHBr_2O_2 + NO \longrightarrow CHBr_2O + NO_2 \quad (11)$$

Two sets of experiments were conducted in the Ford environmental chamber to determine the relative importance of reactions (12), (13), and (14) in the chemistry of $CHBr_2O$ radicals under atmospheric conditions:

$$CHBr_2O + O_2 \longrightarrow COBr_2 + HO_2 \quad (12)$$

$$CHBr_2O + M \longrightarrow HC(O)Br + Br + M \quad (13)$$

$$CHBr_2O + M \longrightarrow BrCO + HBr + M \quad (14)$$

$$BrCO \longrightarrow Br + CO \quad (15)$$

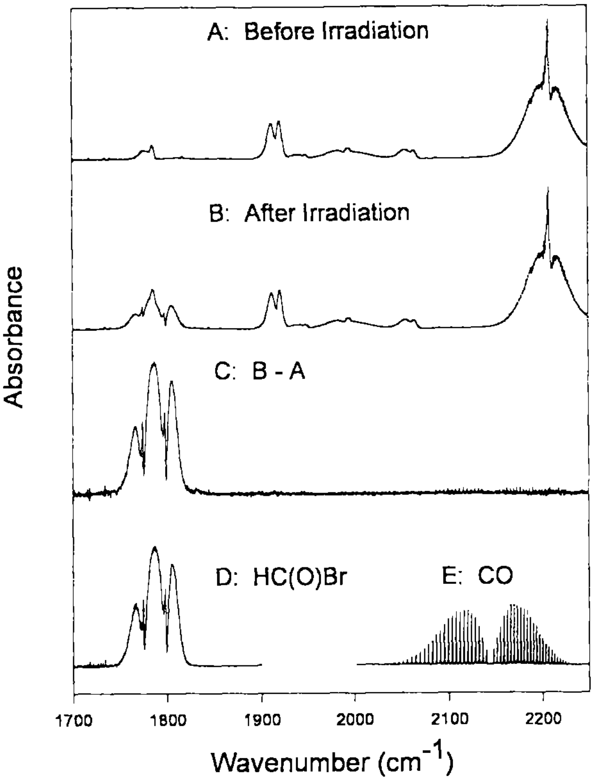

Figure 7 IR spectra taken before and after a 5 second UV irradiation of a mixture of 1.84 torr of CH_2Br_2 and 138 mtorr of Cl_2 in 700 torr of air diluent. Panel C shows the product spectrum (enlarged by a factor of 5) derived by subtracting A from B. Reference spectra of HC(O)Br and CO are displayed.

In the first set of experiments, mixtures of 1.7–1.9 torr of CH_2Br_2, 140 mtorr of Cl_2, and 0–16 mtorr of NO in 700 torr of air diluent were irradiated for 5–45 s using the UV blacklamps. Figure 7 shows IR spectra acquired before (A) and after (B) a 5 s irradiation of a mixture of 1.84 torr of CH_2Br_2 and 138 mtorr of Cl_2 in 700 torr of air diluent. Panel C shows the product spectrum derived by subtracting A from B. Comparison of the product spectrum with reference spectra of HC(O)Br and CO shows the formation of these species. In all experiments, the only two carbon-containing products observed were HC(O)Br and CO. The consumption of CH_2Br_2 was kept low (0.05–0.22%) in the present experiments to minimize secondary removal of HC(O)Br by Cl and/or Br atoms. With such small consumptions it is not possible to directly measure the loss of CH_2Br_2. Assuming for the moment that the observed HC(O)Br and CO products arise from the Cl atom initiated oxidation of CH_2Br_2, the loss of CH_2Br_2 can be equated with the observed formation of HC(O)Br and CO. Figure 8 shows a plot of the observed HC(O)Br and CO concentrations versus the sum of the HC(O)Br and CO concentrations. When reaction mixtures were left to stand in the dark in the chamber the HC(O)Br decayed slowly while the CO increased proportionately. The loss of HC(O)Br followed first order kinetics with a pseudo-first-order rate constant of 0.009–0.015 min^{-1}. This slow loss of HC(O)Br is presumably heterogeneous in nature and is consistent with previous observations in our laboratories and elsewhere [21,33]. The increase in CO concentration on decomposition of HC(O)Br provides a means to calibrate the HC(O)Br IR spectral features [21]. Using this approach, a value of σ(HC(O)Br) at 1805 cm^{-1} = $(1.5 \pm 0.3) \times 10^{-18}$ cm^2 molecule^{-1} was derived in the present work. The quoted uncertainty reflects the precision of the measurements and a 10% systematic uncertainty associated with the CO calibration and IR path length. This result is in good agreement with our previous measurement [21] of $\sigma = (1.7 \pm 0.4) \times 10^{-18}$ cm^2 molecule^{-1}. The filled symbols in Figure 8 are the observed experimental data. The open symbols show the result of correction for the slow loss of HC(O)Br. HC(O)Br was the dominant product observed in all experiments. As is also evident in Figure 8, the addition of NO to the re-

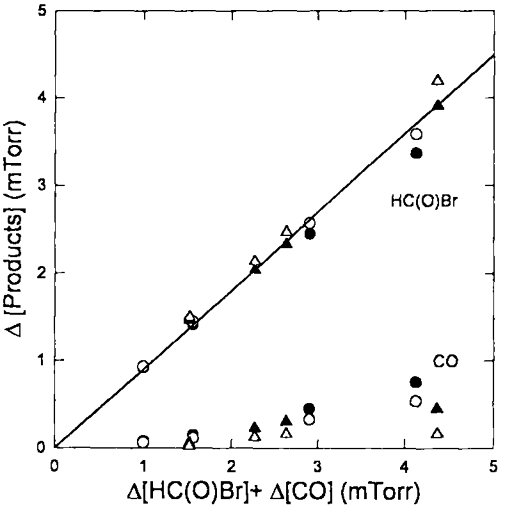

Figure 8 Yields of HC(O)Br and CO versus the sum of the HC(O)Br and CO yields following UV irradiation of mixtures of 1.8 torr of CH_2Br_2 and 0.14 torr of Cl_2 in 700 torr of air, with (triangles) and without (circles) 16 mtorr of NO added. Filled symbols are observed data, open symbols have been corrected for HC(O)Br loss (see text for details). The line is a linear regression through the corrected HC(O)Br data.

action mixtures had no discernible impact on the results obtained. The data shown suggest that following their formation by either the self-reaction of the peroxy radical ($CHBr_2O_2$), or the reaction of $CHBr_2O_2$ with NO, the $CHBr_2O$ radicals predominantly eliminate a Br atom to give HC(O)Br in 700 torr of air at 296 K.

In the above analysis it is assumed that the sum of the observed HC(O)Br and CO products provides an accurate measure of the CH_2Br_2 loss. This assumption will not be valid if the CH_2Br_2 sample contains reactive impurities whose oxidation leads to the formation of these products. Indeed, based upon: (i) the manufacturer's stated CH_2Br_2 purity of >99%; (ii) the low conversions of CH_2Br_2 employed (0.05–0.22%); and (iii) the relatively low reactivity of Cl atoms towards CH_2Br_2, it could be argued that under the experimental conditions pertaining to the data in Figure 8 essentially all of the HC(O)Br and CO comes from reaction of Cl atoms with reactive impurities in the CH_2Br_2 sample. As an experimental check on the consumption of CH_2Br_2, a second set of experiments was performed in which CH_3OCH_3 was added to the reaction mixtures. Chlorine atoms react a factor of 420 (1.9×10^{-10} [34]/4.5×10^{-13}) times faster with CH_3OCH_3 than with CH_2Br_2. By monitoring the loss of CH_3OCH_3 the consumption of CH_2Br_2 can be calculated using expression I. Control experiments were performed by irradiating CH_3OCH_3/Cl_2/air mixtures to check for the formation of HC(O)Br and CO; none was observed.

$$CH_2Br_2\ \text{loss}\ (\%) = 100 \times (1 - \exp((\mathrm{Ln}([CH_3OCH_3]_t/[CH_3OCH_3]_{t0}))/420)) \qquad \text{(I)}$$

Figure 9 shows a plot of the formation of HC(O)Br and CO vs. the calculated loss of CH_2Br_2 following the irradiation of $CH_2Br_2/CH_3OCH_3/Cl_2/O_2/N_2$ mixtures. Filled symbols are the experimentally observed data, open symbols have been corrected for the decay of HC(O)Br. As seen in Figure 9, variation of the O_2 partial pressure over the range 6.7–700 torr had no discernible impact on the measured HC(O)Br and CO yields. Linear least-squares analysis of the HC(O)Br data gives a molar yield (defined as moles of HC(O)Br formed per mole of CH_2Br_2 lost) = 1.13 ± 0.10. The quoted error is two standard deviations from the linear regression, and we estimate that uncertainty associated with the calculation of the loss of CH_2Br_2 could add an additional 20% uncertainty range. Hence, within the experimental uncertainties, HC(O)Br accounts for 100% of the CH_2Br_2 loss.

Two experiments were performed in which NO

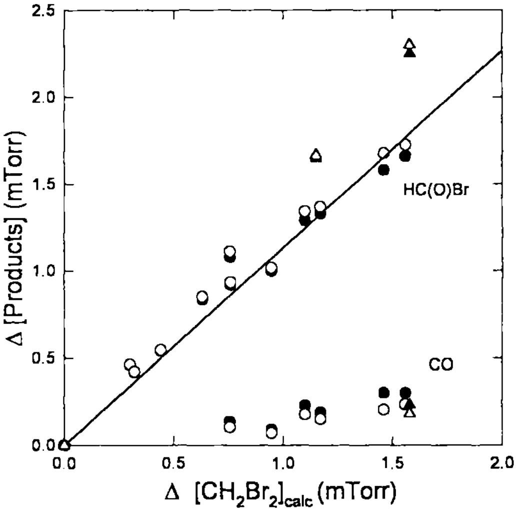

Figure 9 Formation of HC(O)Br and CO versus the loss of CH_2Br_2 following UV irradiation of mixtures of 0.98–1.95 torr of CH_2Br_2, 0.13–0.25 torr of Cl_2, 0.08–0.16 mtorr of CH_3OCH_3, 6.7–700 torr of O_2 at 700 torr total pressure made up with N_2 diluent where appropriate. Triangles are data obtained in the presence of 21.8 mtorr of NO. Filled symbols are the observed data, open symbols have been corrected for HC(O)Br loss (see text for details). The line is a linear regression through the corrected HC(O)Br data (NO experiments excluded).

was added to $CH_2Br_2/Cl_2/CH_3OCH_3$/air mixtures. The results from experiments employing NO are qualitatively consistent with those obtained without NO, i.e., HC(O)Br was the dominant product and small amounts of CO were detected. As shown in Figure 9, the yield of HC(O)Br observed in the presence of NO was larger than that in its absence. Values of $\Delta[CH_2Br_2]$ in Figure 9 were calculated from the observed loss of CH_3OCH_3 using expression I. This calculation assumes that CH_3OCH_3 and CH_2Br_2 are lost solely through reaction with Cl atoms. In the presence of NO, OH radicals are generated by reaction of HO_2 radicals with NO. OH radicals will react with a variety of species present in the chamber, e.g., CH_2Br_2, CH_3OCH_3, NO, NO_2, and HC(O)Br. OH radicals are 24 (2.6×10^{-12}[35,36]/1.1×10^{-13}) times more reactive towards CH_3OCH_3 than towards CH_2Br_2 and are much less discriminating than Cl atoms. Thus, the CH_2Br_2 loss calculated using expression I is an underestimate of the true CH_2Br_2 loss and it is therefore not surprising that the data obtained in the presence of NO lies slightly above the rest of the data in Figure 9.

The data given in Figures 8 and 9 show that under the experimental conditions of the study [296 K, $[O_2] = 6.7-700$ torr, 700 torr total pressure with N_2 diluent) $CHBr_2O$ radicals eliminate a Br-atom to give HC(O)Br. A small yield of CO was also observed. A substantial fraction, but not all, of the observed CO product can be attributed to the decomposition of HC(O)Br. The remaining CO may be attributable to secondary reactions of Cl and/or Br atoms with HC(O)Br. However, we can not rule out a small ($\approx 5\%$) contribution to the $CHBr_2O$ radical loss via intramolecular HBr elimination (reaction (14)), with subsequent production of CO via reaction (15).

A lower limit to the rate of Br-atom elimination from $CHBr_2O$, reaction (13), can be obtained if some assumptions are made regarding the rate coefficient for its reaction with O_2, k_{12}. Rate coefficients for reactions of alkoxy radicals range from about $(2-60) \times 10^{-15}$ cm^3 $molec^{-1}$ s^{-1} [19], and seem to be anti-correlated with the alkoxy C—H bond strength. The C—H bond in $CHBr_2O$ is likely quite weak and hence we estimate $k_{12} \geq 10^{-14}$ cm^3 $molec^{-1}$ s^{-1}. From above, it can be concluded that reaction (13) occurs at least 20 times faster than reaction (12) even in the presence of 700 torr of O_2, which leads to a lower limit for k_{13} of 4×10^6 s^{-1} (for 296 K, 700 torr pressure). This value is consistent with our recent findings for CH_2BrO radicals [21] and with previously reported rate coefficients for Cl atom elimination from alkoxy radicals [37,38].

CONCLUSION

Relative rate techniques were used to obtain rate coefficients for reactions of OH with CH_2Br_2 (at 298 K), and for Cl atoms with CH_2Br_2 and CH_3Br (between 228 and 296 K). The rate coefficient for reaction of OH with CH_2Br_2 was found to be $(1.2 \pm 0.3) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}, in agreement with previous values [16,31]. This determination of the value of k_1 also confirms the short atmospheric lifetime of CH_2Br_2, 0.4 years [16]. Rate coefficients for the reactions of Cl atoms with CH_2Br_2 and CH_3Br were found to be in excellent agreement with the previous measurements of Gierczak et al. [23], but differed from those reported by Tschuikow-Roux et al. [22].

Finally, the elimination of a Br atom, reaction (13), was found to be the dominant fate of the alkoxy radical, $CHBr_2O$, obtained in the atmospheric oxidation of CH_2Br_2. The rate of Br-atom elimination is estimated to be at least 4×10^6 s^{-1} at 298 K and 700 torr total pressure.

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