

The atmospheric degradation of 1-bromopropane (CH₃CH₂CH₂Br): The photochemistry of bromoacetone

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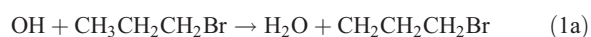
[1] The atmospheric degradation of 1-bromopropane and its degradation products are examined with respect to their ability to deplete stratospheric ozone. It is shown that the OH initiated oxidation of 1-bromopropane does not lead to long lived bromine containing species. Laboratory measurements of the UV absorption cross sections and photodissociation quantum yields of chloroacetone and bromoacetone are presented. The atmospheric photolysis lifetime of bromoacetone at mid-latitudes is determined to be on the order of hours. *INDEX TERMS*: 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation**: Burkholder, J. B., M. K. Gilles, T. Gierczak, and A. R. Ravishankara, The atmospheric degradation of 1-bromopropane (CH₃CH₂CH₂Br): The photochemistry of bromoacetone, *Geophys. Res. Lett.*, 29(17), 1822, doi:10.1029/2002GL014712, 2002.

1. Introduction

[2] 1-bromopropane (CH₃CH₂CH₂Br) has been proposed as a CFC replacement compound. The environmental acceptability of a CFC substitute is evaluated based on its ozone depletion potential (ODP), greenhouse warming potential (GWP), and toxicity. A suitable replacement compound has a short atmospheric lifetime and is efficiently removed in the troposphere following its release at the Earth's surface. However, a comprehensive evaluation of a very short-lived compound also includes consideration of the fate of its atmospheric degradation products and their impact on stratospheric ozone.

[3] *Bridgeman et al.* [2000] and *Wuebbles et al.* [2001] have recently published modeling studies of the ODP for the short-lived 1-bromopropane which has an atmospheric lifetime of ~10 days. Their calculations used literature values for the rate coefficient for the reaction of 1-bromopropane with OH, site specific reactivity based on the empirical reactivity relationships given by *Atkinson* [1986], and assumed degradation products and product lifetimes. These studies demonstrated that it is not possible to define a single ODP value for a short-lived species. The calculations have limitations due to uncertainties in the location and seasonal dependence of the source gas emission and in the mechanism for the degradation of 1-bromopropane.

[4] Recently, we reported rate coefficient and product branching ratios, $\Phi(T)$, for the reaction,



with $\Phi_{1a}(298 \text{ K}) = 0.12 \pm 0.08$, $\Phi_{1b}(298 \text{ K}) = 0.56 \pm 0.04$ and $\Phi_{1c}(298 \text{ K}) = 0.32 \pm 0.08$. [*Gilles et al.*, 2001] In this letter, we evaluate the atmospheric degradation of 1-bromopropane that proceeds through the different product channels. UV absorption cross sections and photodissociation quantum yields for chloroacetone and bromoacetone are presented.

2. Experimental Details

[5] UV absorption cross sections of chloroacetone and bromoacetone were measured using a diode array spectrometer. UV and infrared absorption cross sections were determined simultaneously using two 10 cm long absorption cells in parallel and absolute pressure measured using a 10 Torr capacitance manometer. Infrared measurements were made using a Fourier transform spectrometer at 1 cm⁻¹ resolution. UV absorption cross sections in the long wavelength tail were measured using an absorption cell with a path length of 205 cm. The temperature dependence of the absorption cross sections was measured relative to the simultaneously measured room temperature IR absorption spectrum.

[6] Photodissociation quantum yields for chloroacetone and bromoacetone were determined using a broadband light source (cw fluorescent blacklamps) and pulsed excimer lasers (308 and 351 nm) by monitoring the loss of the parent compound via infrared absorption. Broadband photolysis measurements were made in a 20 L glass reaction cell optically coupled to a Fourier transform infrared spectrometer. The spectral distribution of the fluorescent lamp output was measured using the diode array spectrometer. The lamp emitted between 300 and 400 nm with maximum output at ~350 nm. The photon flux from the lamp was calibrated using NO₂, Cl₂, and CH₂I₂ as reference compounds. Laser photolysis experiments were performed in a 10 cm long absorption cell. The laser fluence was measured using NO₂ as an actinometer. [*Gierczak et al.*, 1998]

3. Results and Discussion

[7] The degradation of 1-bromopropane is initiated by its reaction with OH in the troposphere and stratosphere. H atom abstraction at the three possible reaction sites in this compound will lead to different stable degradation products. The atmospheric fate of these degradation products needs to

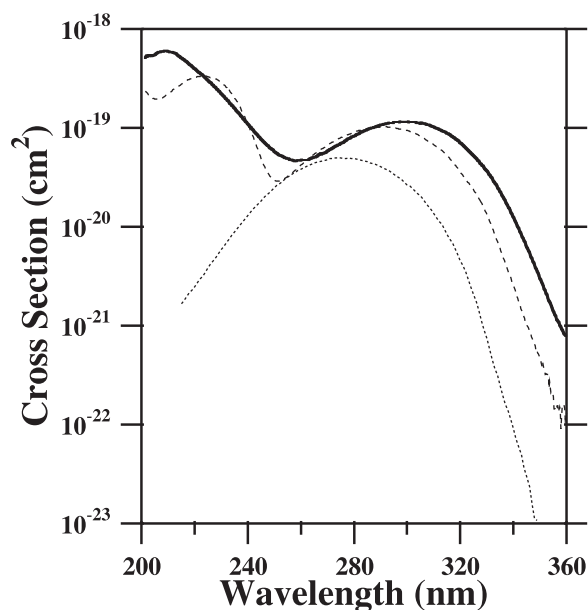


Figure 1. Room temperature absorption spectra of acetone (short dashed line), chloroacetone (long dashed line), and bromoacetone (solid line). The acetone absorption cross section data was taken from *Gierczak et al.* [1998].

be characterized to determine the impact of 1-bromopropane on the stratosphere. Using literature data, analogies with known chemistry of organic molecules and the present work, we have evaluated the atmospheric fate of these degradation products below. A comprehensive diagram of the atmospheric degradation of 1-bromopropane is available in the supplementary material¹.

3.1. Channel 1b: $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{Br}$

[8] Channel (1b) has been determined to be the major reactive pathway in the reaction of OH with 1-bromopropane with a room temperature yield of 56%. [*Gilles et al.*, 2001] We also observed bromoacetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{Br}$, to be the major stable product formed following reaction (1b). Quantitative information on the photochemistry and kinetics of bromoacetone is very limited. [*Kash et al.*, 1994]. Therefore, we measured the UV absorption cross sections and photolysis quantum yields for bromoacetone to quantify this atmospheric loss process. We have also performed similar measurements for chloroacetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{Cl}$, for comparison purposes and the evaluation of its atmospheric lifetime.

3.1.1. UV absorption cross sections

[9] The room temperature absorption spectra of acetone, chloroacetone, and bromoacetone are shown in Figure 1. The halogenated ketones show a red-shift and an increase in the peak cross section value near 300 nm from that of acetone. *Kash et al.* [1994] have published a room temper-

ature absorption spectrum of bromoacetone but did not report absorption cross sections. Their spectrum is in qualitative agreement with ours with the largest differences being in the spectral shape observed at the short wavelengths. The uncertainty in our measured absorption cross sections is wavelength dependent and we estimate the 2σ uncertainties to be $\pm 15\%$ at 290 nm increasing to $\pm 25\%$ at 340 nm.

[10] Absorption cross sections were measured between 296 and 243 K. A systematic decrease in the absorption cross sections with decreasing temperature was observed at wavelengths greater than 290 nm. For example, the chloroacetone absorption cross section at 320 nm decreased by $\sim 20\%$ between 296 and 243 K. Including the temperature dependence of the absorption cross sections will result in slightly smaller calculated atmospheric photolysis rates. The UV cross section data at 296, 273, 253, and 243 K along with 296 K IR data are provided in the supplementary material¹.

3.1.2. Photodissociation quantum yields

[11] There are several energetically allowed channels available for the atmospheric photolysis ($\lambda > 290$ nm) of bromoacetone. Photodissociation leads to either the immediate release of Br, or its rapid release following the oxidation of the CH_2Br radical and the thermal decomposition of the BrH_2CO radical. In this work, we did not identify the specific photolysis channels for bromoacetone but have determined its photodissociation quantum yield (i.e., loss of bromoacetone).

3.1.2.1. Broadband photolysis

[12] Measured rates of bromoacetone removal were compared with the rates calculated from the overlap of the lamp spectrum and the absorption cross sections. The measured first order photolysis rate coefficients for the reference compounds NO_2 , Cl_2 , and CH_2I_2 were $4 \times 10^{-3} \text{ s}^{-1}$, $1.3 \times 10^{-3} \text{ s}^{-1}$, and $2.7 \times 10^{-3} \text{ s}^{-1}$, respectively. The ratio of the measured loss rate coefficients for NO_2 and Cl_2 are in excellent agreement, within 5%, with the calculated values. The loss rate coefficient for CH_2I_2 , however, was $\sim 40\%$ higher than that predicted using the measured NO_2 loss rate coefficient. This difference may reflect the uncertainty in the photolysis lamp flux at the shorter wavelengths.

[13] Chloroacetone and bromoacetone had slow, $1.6 \times 10^{-5} \text{ s}^{-1}$, loss rate coefficients in the absence of photolysis. The measured (uncorrected for dark loss) first order loss rate coefficients for chloroacetone and bromoacetone during photolysis were $(3.2 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$ and $(5.7 \pm 1.0) \times 10^{-5} \text{ s}^{-1}$, respectively. The photolysis rate coefficients were independent of the total cell pressure between 50 and 600 Torr of air. The concentrations of CO and CO_2 produced were ~ 0.5 of the chloroacetone or bromoacetone lost. HCl and HBr were not observed; their yield is estimated to be < 0.05 and < 0.2 , respectively. Some weak but unidentified absorption features in the carbonyl stretch region were also observed.

[14] The chloroacetone and bromoacetone photodissociation rate coefficients are, respectively, 25% and 50% higher than the rate coefficients calculated relative to the NO_2 actinometry. As in the case of CH_2I_2 , the larger value may indicate a systematic underestimate of the short wavelength flux from the lamp or the possible loss of bromoacetone and chloroacetone due to secondary chemistry. These measurements, although limited in accuracy, indicate that

¹Auxiliary material (Figures 2 and 3 and Table 1) is available via Web browser or via Anonymous FTP from <ftp://kosmos.agu.org>, directory "append" (Username = "anonymous", Password = "guest"); subdirectories in the ftp site are arranged by paper number. Information on searching and submitting electronic supplements is found at http://www.agu.org/pubs/esupp_about.html.

the quantum yields for atmospheric photodissociation are significant; we conservatively estimate them to be >0.5 .

3.1.3. Laser photolysis

[15] The photolysis quantum yields, $\Phi(\lambda, X)$, for the loss of a molecule were calculated using:

$$\Phi(\lambda, X) = \ln([X]/[X]_0) / (n\sigma(\lambda, X)F) \quad (2)$$

where X is either chloroacetone, bromoacetone, or NO_2 , $\sigma(\lambda, X)$ is the absorption cross section of X at the photolysis wavelength, λ , and F is the laser fluence in units of photons $\text{cm}^{-2} \text{pulse}^{-1}$ at λ . The laser fluences at 308 and 351 nm were 1.0×10^{16} photons $\text{cm}^{-2} \text{pulse}^{-1}$ and 7.5×10^{15} photons $\text{cm}^{-2} \text{pulse}^{-1}$ ($\pm 10\%$), respectively.

[16] The photodissociation quantum yields were determined to be 0.5 ± 0.08 and 1.0 ± 0.15 at 351 nm and 0.5 ± 0.08 and 1.6 ± 0.25 at 308 nm for chloroacetone and bromoacetone, respectively. The quoted uncertainties are the 2σ limits from the fit to the compounds measured loss. Uncertainties in the infrared absorption cross sections and spectral subtractions will also contribute to the uncertainties in the quantum yields. We estimate the uncertainty in the absolute values to be 25% and 50% at 308 and 351 nm, respectively. The bromoacetone quantum yield at 308 nm did not change upon the addition of an OH radical scavenger (ethane) to the gas mixture. The source of the higher than unity values is currently not known, but may be due to the combined uncertainties in absorption cross sections, laser fluence and unaccounted for homogeneous or heterogeneous secondary chemistry.

[17] Formic acid (HC(O)OH), CO , CO_2 , HCl , and HBr were observed as photolysis products. For bromoacetone, the CO quantum yield was near unity at both 308 and 351 nm while the CO_2 quantum yield was ~ 0.5 . The formic acid yield was small, <0.15 . HBr was observed with a yield of ~ 0.15 . For chloroacetone, the CO quantum yield was ~ 0.5 at both 308 and 351 nm. The CO_2 yield was ~ 0.25 while the formic acid and HCl yields were 0.25 and 0.50, respectively. CH_2O was not observed, <0.1 yield. Based on these studies, we conclude that the quantum yield for the dissociation of bromoacetone is >0.5 in the actinic region.

[18] Based on the measured cross sections and quantum yields, the atmospheric photolysis lifetimes of chloroacetone and bromoacetone are on the order of hours during daytime at mid-latitudes. Reactive losses of these compounds are not expected to contribute significantly to their atmospheric removal. Quantitative identification of photolysis products along with measurements of the wavelength, pressure, and temperature dependence of the quantum yields for chloroacetone and bromoacetone removal would be desirable. In the absence of such information, we estimate that the tropospheric photolysis will yield Br or a product that quickly releases Br (see Supplementary material, Figure 2)¹.

3.2. Channel 1c: $\text{CH}_3\text{CH}_2\text{C(O)H}$

[19] The yield of channel (1c) has been determined to be 32% at 298 K. [Gilles *et al.*, 2001] Following reaction (1c), bromine is rapidly released with the simultaneous formation of propanal. The formation of peroxy nitrates and hydroperoxy compounds from the $\text{CH}_3\text{CH}_2\text{CHBr(OO)}$ radical reactions with NO_2 and HO_2 represent minor

channels. Therefore, the reaction of OH at the $-\text{CH}_2\text{Br}$ site in 1-bromopropane will rapidly release bromine into the atmosphere.

3.3. Channel 1a: $\text{BrCH}_2\text{CH}_2\text{C(O)H}$

[20] Reaction channel (1a) is a minor channel with a yield of 12%. [Gilles *et al.*, 2001] In the troposphere the degradation of the $\text{BrCH}_2\text{CH}_2\text{CH}_2$ radical leads primarily to the formation of $\text{BrCH}_2\text{CH}_2\text{C(O)H}$. The formation of the peroxy nitrates, $\text{O}_2\text{NOOCH}_2\text{CH}_2\text{CH}_2\text{Br}$, and hydroperoxide, $\text{HOOCH}_2\text{CH}_2\text{CH}_2\text{Br}$, will depend on the atmospheric concentrations of NO_2 and HO_2 relative to NO and are expected to be only minor pathways. Furthermore, these compounds are not expected to have long atmospheric lifetimes. These compounds have not been specifically studied in the laboratory but peroxy nitrates in general are thermally unstable over the range of temperatures found in the troposphere, with lifetimes of minutes. [Zabel *et al.*, 1994] Bromine atom substitution is not expected to significantly alter the thermal decomposition rates. Hydroperoxy compounds are removed from the atmosphere by UV photolysis, OH reaction, and wet deposition. Wet deposition may dominate the removal process with a lifetime of 5 to 10 days and would lead to the direct removal of reactive bromine from the atmosphere. The OH reaction will lead to the reformation of the $\text{OOCH}_2\text{CH}_2\text{CH}_2\text{Br}$ radical or other products depending on where along the carbon chain the reaction occurs. UV photolysis of $\text{HOOCH}_2\text{CH}_2\text{CH}_2\text{Br}$ will likely lead to the formation of the $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Br}$ radical or, possibly, to the direct elimination of the bromine atom. In summary, UV photolysis of $\text{HOOCH}_2\text{CH}_2\text{CH}_2\text{Br}$ and its reaction with OH will primarily lead to the formation of $\text{BrCH}_2\text{CH}_2\text{C(O)H}$; small yields of other bromine containing compounds are also possible.

[21] The atmospheric degradation of $\text{BrCH}_2\text{CH}_2\text{C(O)H}$ formed subsequent to reaction (1a) is outlined in the supplement. The degradation mechanism was constructed by analogy with the degradation of short chain organic aldehydes, which have been extensively studied. However, the addition of a weak C-Br bond to the molecule increases the number of possible decomposition and photolysis channels. We have tried to include all the reasonable reaction pathways initiated by UV photolysis and OH reaction. The reaction with OH is expected to be rapid, with a lifetime of one day. The UV photolysis of this aldehyde should also be rapid. OH reaction or UV photolysis at the $-\text{C(O)H}$ group leads to the formation of another aldehyde which still contains bromine but with one less carbon atom. PAN type peroxy nitrates, RC(O)OONO_2 , may also be formed in small amounts. Although these nitrate compounds are minor products, they are of interest due to their longer lifetimes, ~ 1 month. [Talukdar *et al.*, 1995], in the upper troposphere. UV photolysis may also lead to the direct elimination of a bromine atom. Laboratory studies of the photolysis products and quantum yields of $\text{BrCH}_2\text{CH}_2\text{C(O)H}$ would aid this analysis.

[22] We conclude that $\text{BrCH}_2\text{CH}_2\text{C(O)H}$ would be removed from the troposphere within a day of sunlight via reaction with OH and UV photolysis. The majority of the products formed from its degradation would also be rapidly removed with the exception of $\text{HOOCH}_2\text{CH}_2\text{CH}_2\text{Br}$. This compound, if formed, will be a small fraction of the

BrCH₂CH₂C(O)H. Even this compound is expected to be removed from the atmosphere within a few days.

4. Atmospheric Implications

[23] Atmospheric lifetimes and ozone depletion potentials (ODPs) are calculated by assuming uniform mixing of the compound in the troposphere. For short-lived compounds such as 1-bromopropane that has an atmospheric lifetime of ~10 days, the assumption of uniform mixing in the troposphere breaks down and the traditional approach of calculating ODPs becomes less meaningful. This point has been illustrated in two recent model calculations. *Bridgeman et al.* [2000] showed the sensitivity of stratospheric ozone depletion for a short-lived compound to its location (mixing time dependence) and season (tropospheric loss rate dependence) of its emission. Their calculations assumed immediate release of Br following the loss of 1-bromopropane via OH reaction. *Wuebbles et al.* [2001] extended this idea using a 3D model by including a 1-bromopropane degradation mechanism (similar to that presented in this paper) and accounting for contributions from the degradation products. They concluded that the degradation products make a significant contribution to the overall calculated ozone depletion and therefore need to be included.

[24] The major products following the OH initiated degradation of 1-bromopropane in the atmosphere, the major pathway for the loss of this compound, are bromoacetone, propanal (with Br as a co-product) and 3-bromopropanal. Our work has shown that bromoacetone will rapidly photolyze to eventually release Br and will be very short-lived. Since bromoacetone and propanal account for nearly 90% of the 1-bromopropane that is destroyed, it appears that the major fate of the atmospheric degradation of 1-bromopropane in the troposphere is to rapidly and irreversibly release bromine atoms. A small fraction of 1-bromopropane degradation in the troposphere may lead to a bromine-containing compound via the formation of 3-bromopropanal (and its degradation) that could have lifetimes of a few days. The major difference between our conclusions and the input parameters for the previous modeling studies is the lifetime of bromoacetone. We show that the lifetime is short, perhaps hours, while it was previously assumed to be weeks. Therefore, the previous estimate of Wuebbles et al. on the impact of 1-bromopropane

on stratospheric ozone are overestimated, if we assume that the inorganic bromine is removed by precipitation at the rates assumed in these models.

[25] An estimation of the contribution of tropospheric Br to the stratosphere critically depends on the tropospheric chemistry of bromine, the location of its release, and the transport characteristics of this region. The key uncertainty is the rate at which inorganic bromine is irreversibly removed via precipitation. Unfortunately, the fate of the Br released into the troposphere, especially the upper troposphere, and its ability to reach the stratosphere depends on factors that are not well quantified at this time.

[26] **Acknowledgments.** This work was supported in part by the NOAA climate and global change program. We thank D. Albritton for helpful discussions.

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