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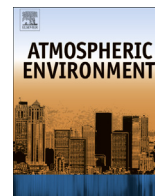


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Re-evaluation of the reaction rate coefficient of $\text{CH}_3\text{Br} + \text{OH}$ with implications for the atmospheric budget of methyl bromide

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HIGHLIGHTS

- Reaction rate for $\text{CH}_3\text{Br} + \text{OH}$ determined using absolute and relative rate techniques.
- The results of the present study give faster rates than current recommendations.
- The results imply that the imbalance between sources and sinks of the methyl bromide budget is larger than previously thought.

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ABSTRACT

The reaction rate coefficient $k(\text{CH}_3\text{Br} + \text{OH})$ has been determined in the temperature range 298–373 K, using pulse radiolysis/UV kinetic spectroscopy, and at 298 K using a relative rate method. The Arrhenius expression obtained from a fit to the experimental results is $(2.9 \pm 0.9) \times 10^{-12} \exp(-(1230 \pm 125)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is greater than the expression currently recommended. The relative rate experiments give $k(298 \text{ K}) = (4.13 \pm 0.63) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The results of the absolute and relative rate experiments indicate that the source budget of atmospheric CH_3Br should be reinvestigated, as was recently done for CH_3Cl .

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1. Introduction

Research on halogenated compounds is largely driven by their role in catalytic cycles removing stratospheric ozone (WMO, 2010). Chlorine is the most abundant halogen in the atmosphere, originating from HFCs (hydrofluorocarbons) and CFCs (chlorofluorocarbons). Bromine is present at lower concentrations, but due to the relatively greater reactivity of its reservoir compounds bromine is a more efficient catalyst, removing an order of magnitude more ozone per atom than chlorine (Holloway and Wayne, 2010). Bromine is implicated in Arctic mercury and ozone depletion events (Douglas et al., 2012).

Methyl bromide, CH_3Br , is the most important bromine source in the atmosphere; it is emitted by both natural and anthropogenic sources (Warwick et al., 2006). Methyl bromide has been widely used as a fumigant, but was restricted under the Montreal protocol, and its release from anthropogenic sources has therefore decreased in recent years. The current knowledge about the atmospheric

budget of methyl bromide has been reviewed in “Scientific Assessment of Ozone Depletion 2010” (WMO, 2010). The dominant natural source is the oceans, producing an estimated 42 (34–49) Gg CH_3Br every year. In the period 1996–1998 annual production of CH_3Br for fumigation was as high as the ocean source, while in recent years it has declined to about one sixth. Today the second most important source is biomass burning contributing with about 29 (10–40) Gg year^{-1} (WMO, 2010). The budget includes significant uncertainties; based on current knowledge the three main loss processes (ocean, soil and in situ chemistry) remove about 20% more CH_3Br than the sources produce. Chemical removal from the atmosphere is the most important loss process (WMO, 2010). The main atmospheric oxidant is OH, and this is the main loss process in the troposphere. In the cold and dry conditions of the stratosphere removal by $\text{O}(^1\text{D})$ atoms is also important, as is photolysis.

Modeling has shown that the imbalance in the atmospheric budget of methyl bromide is most likely due to missing sources (Yvon-Lewis et al., 2009). Several scenarios were modeled by Yvon-Lewis et al. (2009), including a reduction in the chemical loss rate which resulted in discrepancies concerning seasonal variations. Based on analysis of the scenarios it was concluded that the most likely explanation for the imbalance is a missing source or sources.

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Abiotic production of methyl bromide through the temperature dependent breakdown of plant material has not been quantified; recent work has shown that this process may be important in tropical forests (Wishkerman et al., 2008). Methyl chloride is known to be produced in a similar manner and the source budget of methyl chloride was recently increased by a factor of two based on kinetic and isotopic evidence (Gola et al., 2005; Saito and Yokouchi, 2008).

Atmospheric in situ loss of methyl bromide is mainly determined by its reaction with OH (Reaction R1). The reaction rate coefficient for R1 has been determined several times, the results are summarized in Table 1. There is significant scatter in the reported values. At 298 K the rate coefficients span the range 2.60×10^{-14} (Mellouki et al., 1992) to 4.57×10^{-14} (Davis et al., 1976) $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ when uncertainty limits are included.



In this paper we present results of determinations of the second order rate constant for the reaction of OH with methyl bromide over the temperature range 298–373 K, using pulse radiolysis combined with UV kinetic spectroscopy, and relative rate experiments at 298 K.

2. Kinetic experiments

2.1. Absolute rate experiments

The apparatus and experimental procedure for the pulse radiolysis experiments combined with UV kinetic spectroscopy for OH detection have been described in detail elsewhere (Hansen et al., 1979; Nielsen et al., 1989). The irradiation cell is a 1 l stainless-steel cell mounted onto the Febretron 705B field emission accelerator used to generate single pulses of 2 MeV electrons of 30 ns duration. Reaction mixtures consisted of 1.0–8.5 mbar CH_3Br (Gerling and Holz 99%), 15 mbar H_2O (triply distilled) and Argon (AGA 99.9%) to a total pressure of about 1000 mbar. Partial pressures were determined using MKS Baratron 170 absolute membrane manometer with a resolution of 0.1 mbar. The analyzing light source was a pulsed 150 W high pressure xenon arc lamp. A Hilger and Watts grating spectrograph, a Hamamatsu photomultiplier and a Biomation-8100 waveform digitizer were used to detect and record the light intensity. The temperature was measured using a chromel–alumel thermocouple placed in the center of the reaction cell.

To check for interference from reaction products, experiments were conducted in which the same sample was repeatedly pulsed. OH decay was insensitive to at least ten pulses which mean interference from products was not significant.

OH radicals were detected by their transient absorbance at 309 nm, using a modified version of Beer's law, $A = (n \sigma l)^m$, which is required as the spectral band pass is wide compared to the spectral features. The value of m was determined from the function $\log(A) = m(\log(n \sigma l))$ by varying the optical path length. For a spectral band pass of 0.08 nm, m was determined to be 0.70 ± 0.04 . The experimental error in the determination of m introduces an error of approximately 3% in the pseudo first-order rate.

The radiolysis pulse excites Ar atoms which rapidly react with H_2O to form OH radicals. Decay of OH is significantly slower than production and proceeds via Reactions R1, R2 and R3 where the third body M is Ar or H_2O .



To a good approximation the OH decay is described by a differential Equation (1).

$$-\frac{d[\text{OH}]}{dt} = k_1[\text{CH}_3\text{Br}][\text{OH}] + 2k_2[\text{OH}]^2[\text{M}] + k_3[\text{H}][\text{OH}][\text{M}] \quad (1)$$

In the present study the concentration of methyl bromide is large enough to be the dominating loss process, $k_1[\text{CH}_3\text{Br}] \gg 2k_2[\text{OH}][\text{M}] + k_3[\text{H}][\text{M}]$, and therefore pseudo first order conditions apply.

$$\ln\left(\frac{[\text{OH}]_0}{[\text{OH}]_t}\right) = k_1[\text{CH}_3\text{Br}]_t = k'_t \quad (2)$$

A plot of k' versus $[\text{CH}_3\text{Br}]$ is nearly linear with the slope equal to k_1 . The data at each temperature are plotted in Fig. 1 and the value on the resulting slopes, i.e. k_1 , are presented in Table 2.

2.2. Relative rate experiments

The photochemical reactor at the Copenhagen Center for Atmospheric Research consists of a 100 l cylindrical quartz reaction chamber with multipass optics. The composition of the gas mixture was monitored using a Bruker IFS 66v/s FTIR spectrometer. The setup is described in detail elsewhere (Nilsson et al., 2009). Experiments were performed by exposing mixtures of reactant, reference compound and ozone to UVC light with a strong emission at 254 nm. At these wavelengths ozone is photolyzed to produce mainly excited oxygen atoms, Reaction R4. If water concentrations are sufficient the main fate of the excited oxygen atom will be reaction to produce OH radicals, R5. Another possible reaction is recombination with oxygen molecules to form ozone.

Table 1

Summary of available literature data, from experimental studies and data compilations. $k(T) = A \times 10^{-12} \exp(-E_a/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

$k(298 \text{ K}) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$A \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	E_a/K	$T \text{ range K}$	Method ^b	Reference
4.14 ± 0.43	0.79 ± 0.08	889 ± 59	244–350	FP – RF	(Davis et al., 1976)
3.5 ± 0.8			296	DF – LMR	(Howard and Evenson, 1976)
2.96 ± 0.36	2.35	1300 ± 150	233–379	LP – LIF	(Mellouki et al., 1992)
3.08 ± 0.46	5.79	1560 ± 150	250–400	FP – RF	(Zhang et al., 1992)
3.27 ± 0.50	1.86 ± 0.48	1230 ± 150	248–390	DF – EPR	(Chichinin et al., 1994)
2.94 ± 0.09^a	4.4^a	1507^a	298–360	RR	(Hsu and Demore, 1994)
2.9 ± 0.1	1.7	1215 ± 150	240–300	Data evaluation	(Atkinson et al., 2006)
3.0 ± 0.3	2.35	1300	200–300	Data evaluation	(Sander et al., 2011)
4.9 ± 0.5	2.9 ± 0.9	1230	298–373	PR-KS	Present work
4.13 ± 0.63			298	RR	Present work

^a Recalculated using the currently recommended Arrhenius expression for recalculation of relative rate studies involving the reference reaction, $k(\text{CH}_3\text{CHF}_2 + \text{OH}) = 2.33 \times 10^{-12} \exp(-1260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, (Sander et al., 2011).

^b Abbreviations: PR-KS: Pulse Radiolysis – Kinetic Spectroscopy; DF-LMR: Discharge Flow – Laser Magnetic Resonance; FP – RF: Flash Photolysis – Resonance Fluorescence; LP-LIF – Laser Photolysis – Laser Induced Fluorescence; EPR – Electron Paramagnetic Resonance; RR: Relative Rate.

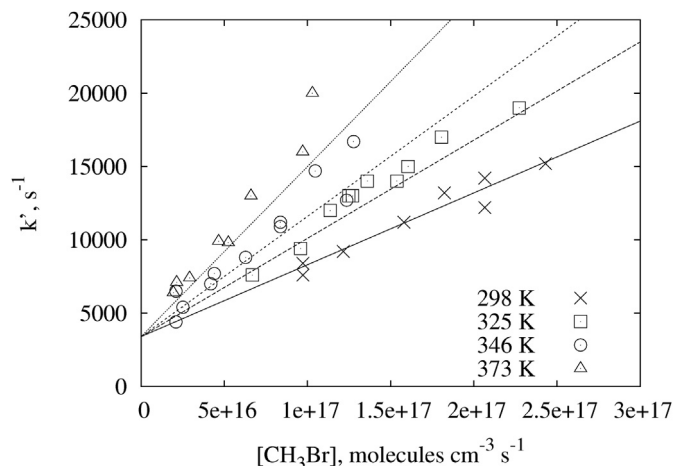


Fig. 1. Plots of k' vs $[\text{CH}_3\text{Br}]$ from the pulse radiolysis absolute rate experiments at the four investigated temperatures. The solid lines are linear least squares fits to the data.

Ozone was generated from O_2 using an ozone generator (Model AC-20, O_3 Technology), preconcentrated before injection on silica gel cooled with ethanol and dry ice to ca. -67°C . The flask containing the silica gel was connected via Teflon and stainless steel tubing to the reaction chamber, and O_3 was drawn into the reaction chamber by vacuum.



The reference compounds used have clear infrared features and well-characterized reaction rate coefficients, $k_6 = (6.30 \pm 0.63) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_7 = (2.50 \pm 0.18) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Sander et al., 2011):



Experiments were performed at $298 \pm 0.5 \text{ K}$. The reaction mixtures were typically photolyzed in 6–15 steps of 10–30 s. An FTIR spectrum consisting of 32 coadded interferograms recorded at a resolution of 0.125 cm^{-1} was obtained after each step. The mixtures were allowed to stabilize for 2 min after each photolysis step. Partial pressures were in the range 0.002–0.03 mbar for reactants and reference compounds, 3.1–3.9 mbar for ozone, 0.4–0.7 mbar for water, and the total chamber pressure was 990 mbar.

Control experiments were performed to check for possible loss of reactants and reference compound in the chamber in the absence of UV irradiation. There was no ($<1\%$) loss of reactants or reference compounds when reaction mixtures were left to stand in the dark for 30 min, the duration of a typical experiment. In addition, no loss of the compounds was seen when mixtures of the gases were irradiated in the absence of O_3 .

Table 2
Reaction rates from the pulse radiolysis experiments at the four investigated temperatures.

$T \text{ (K)}$	$k \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
298	4.9 ± 0.5
325	6.7 ± 0.6
346	8.2 ± 0.8
373	11.6 ± 1.2

The spectra were analyzed using an iterative nonlinear least squares fitting procedure (Griffith, 1996). Reference spectra of CH_3Br , C_2H_6 , CH_4 , O_3 and H_2O were taken from the HITRAN database (Rothman et al., 2009). Spectra were analyzed in the region $1270\text{--}1390 \text{ cm}^{-1}$ for H_2O , O_3 , CH_3Br and CH_4 , and in the region $2973\text{--}3000 \text{ cm}^{-1}$ for C_2H_6 .

The relative rate method is an established method for measuring reaction rates. Kinetic data are derived by monitoring the loss of the reactant and the reference compound. $\ln([\text{reactant}]_{t_0}/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_{t_0}/[\text{reference}]_t)$ was plotted using the expression:

$$\ln\left(\frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t}\right) = \frac{k_{\text{react}}}{k_{\text{ref}}} \ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right) \quad (3)$$

Where $[\text{reactant}]_{t_0}$, $[\text{reactant}]_t$, $[\text{reference}]_{t_0}$ and $[\text{reference}]_t$ are the concentrations of reactant and reference at times t_0 and t , and k_{react} and k_{ref} are the rate constants for reactions of OH with the reactant and reference. Plots of $\ln([\text{reactant}]_{t_0}/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_{t_0}/[\text{reference}]_t)$ should be linear, pass through the origin and have a slope of $k_{\text{react}}/k_{\text{ref}}$. Two experiments were performed with each of the reference compounds, the relative rate plots are shown in Fig. 2. The linear fit to the data was performed on the two datasets for each reference compound together, this procedure give the relative rates $k_1/k_6 = (6.314 \pm 0.146)$ and $k_1/k_7 = (0.175 \pm 0.004)$, represented by the lines in Fig. 2. Errors for the relative rates are based on the asymptotic standard error of the fit. From the relative rates values of k_1 , $(3.99 \pm 0.49) \times 10^{-14}$ and $(4.31 \pm 0.45) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, were calculated using the previously mentioned values of k_6 and k_7 . The errors on these values include the uncertainties in the rates of the reference reactions. Combining these values yield a final result $k_1 = (4.13 \pm 0.63) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3. Discussion

Fig. 3 presents all available experimental data published for the title reaction. The full drawn line in the figure is from the most recent data evaluation (Sander et al., 2011), with uncertainty limits enclosed by the dashed lines. As can be seen from the figure the results from the absolute rate study of the present work are significantly greater than the current recommendation, but within the uncertainty limits. The recommendation is based on data by Hsu and Demore (1994), Zhang et al. (1992) and Chichinin et al. (1994). The data by Chichinin et al. and Zhang et al. show

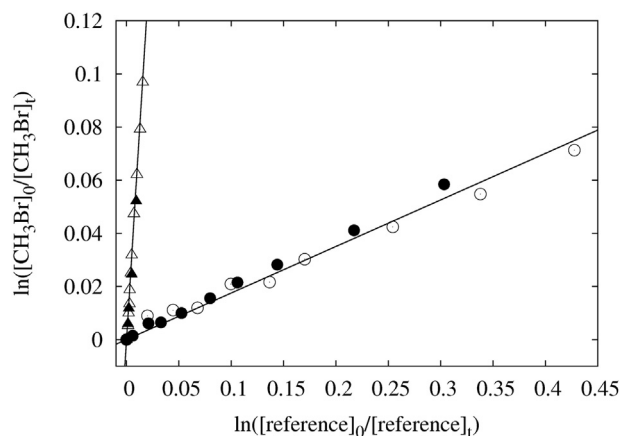


Fig. 2. Relative rate plots for the experiments at 298 K. Reference compounds are C_2H_6 (circles) and CH_4 (triangles). Each dataset consist of results from two separate experiments, distinguished by filled and non-filled symbols.

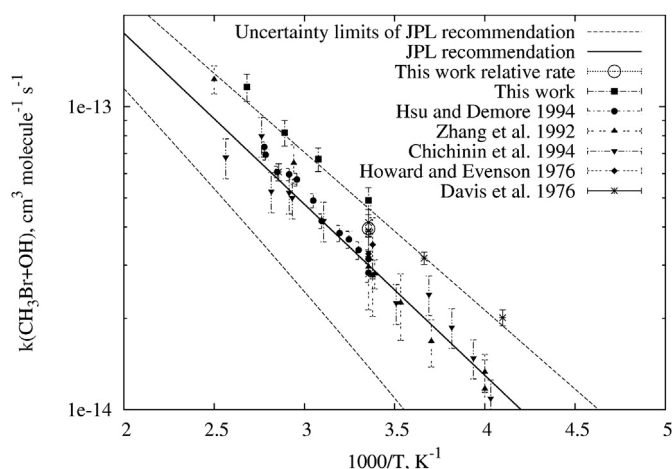


Fig. 3. Arrhenius plot of experimental data from several experimental studies, and the line representing the expression currently recommended by JPL (Sander et al., 2011).

significant scatter, while the relative rate study by Hsu and DeMore is less scattered and has smaller errors. When comparing the shape of the different datasets it is seen that the present data show the same trend as Hsu and DeMore. Their study is a relative rate study, with HFC152a as the reference compound, which mean that the quality of the absolute value of the reaction rate constant depends on the accuracy of the value of the rate constant for the reference reaction. The Hsu and DeMore data presented in the figure were recalculated using the most recent recommendation for the reference reaction ($\text{HFC152a} + \text{OH}$); for information on the expression used in the recalculation we refer to the comment in JPL data evaluation (Sander et al., 2011). It is interesting to note that in earlier data evaluations the recommended $\text{CH}_3\text{Br} + \text{OH}$ reaction rate is closer to the results in the present study.

The Arrhenius expression derived from experimental data in the different studies is presented in Fig. 4 together with the JPL recommendation and the expression obtained in the present work. It is obvious that the slopes of the lines vary significantly between the different studies.

4. Atmospheric implications

The results of the present study suggest that the reaction of methyl bromide with hydroxyl radicals is about 25% faster than the

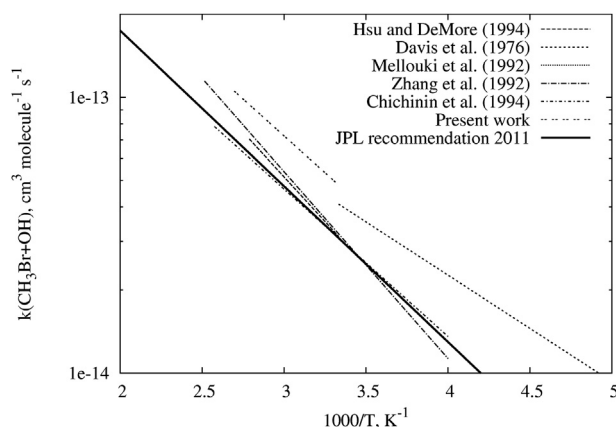


Fig. 4. Lines represent Arrhenius expressions obtained in the different previous studies and in the present work. Thicker line is the JPL recommendation, same as in Fig. 3.

current recommendations. Since chemical removal is the main sink for methyl bromide in the troposphere, estimated at $63.6 \text{ Gg year}^{-1}$ in 2008, a significant increase of the reaction rate implies that the imbalance between sources and sinks is even larger than in the current budgets (WMO, 2010; Yvon-Lewis et al., 2009).

To get a feeling for the impact a faster reaction rate would have on the atmospheric concentration of methyl bromide one can estimate the lifetime of the compound using the simple relation $\tau = 1/(k[\text{OH}])$. The global average OH concentration, $1 \times 10^6 \text{ molecules cm}^{-3}$, determined by Prinn et al. (1995) was used. A lifetime of 1.1 years was obtained using the value of k currently recommended by JPL (Sander et al., 2011), while the results of the present study give a lifetime of about 0.8 years.

As mentioned in the introduction Yvon-Lewis et al. have shown that the imbalance in the methyl bromide budget is not likely due to an overestimation of the sinks, but rather is the result of a missing source. The budget of methyl bromide contains a few unquantified sources (WMO, 2010), one of them being abiotic formation from vegetation (Wishkerman et al., 2008). It has been shown that the release of methyl bromide from plant material is dependent on temperature and bromine content, just as abiotic methyl chloride production depends on temperature and chlorine content (Derendorp et al., 2012). From a study of leaf litter from a temperate forest it was concluded that the release of methyl bromide from that type of vegetation would not contribute significantly on a global scale (Blei and Heal, 2011), but due to the temperature dependence of the abiotic mechanism, it is likely that the process is more important in warmer climates (Yvon-Lewis et al., 2009). A study on leaf litter and live plant branches of selected species in a tropical forest indicate that its contribution to global CH_3Br emission is minor (Blei et al., 2010), but in the same work it is emphasized that data are sparse and scale up is simplistic. Apparently the emission vary significantly between species and only few species have been studied this far.

In conclusion the present work implies that the discrepancy in the atmospheric budget of methyl bromide is larger than previously thought. Based on recent studies it seems likely that at least part of the missing source is due to abiotic production, by analogy with methyl chloride.

The faster reaction rate determined here will result in an overall shorter lifetime for methyl bromide in the atmosphere. Further modeling studies are necessary to investigate the effect on a smaller spatial and temporal scale where fluctuations in OH concentrations are significant.

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