Journal of Environmental Sciences Vol. 9, No. 4, pp. 480—485, 1997 ISSN 1001—0742

Kinetics for the reaction of hydroxyl radicals with CH_3Br and its implications in the atmosphere*

Zhang Deqiang, Zhong Jinxian**

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Qiu Lianxiong

Graduate School of the University of Science and Technology of China, Beijing 100039, China

Abstract—Rate constants for the reaction of hydroxyl radicals with methyl bromide have been measured by the discharge flow-resonance fluorescence (DF-RF) technique over the temperature range 288-351K. The derived Arrhenius equation is: $k'' = (3.42 \pm 0.12) \times 10^{-12} \exp(-(1419 \pm 158)/T)$ $cm^3/(mol \cdot s)$. The tropospheric lifetime of methyl bromide was estimated to be 1.60 years. An ODP value of 0.33 for methyl bromide was obtained.

Keywords: hydroxyl radicals; methyl bromide; discharge flow-resonance fluorescence; atmospheric lifetime; ODP.

1 Introduction

Methyl bromide is an important bromine-containing for ozone destroy substances (ODS) in the atmosphere. Its source from mankind release is mainly agricultural use as soil fumigant and pesticide. Khalil *et al*. derived an annual increase of (3 ± 1)% for the global CH_3Br content in the atmosphere during 1988—1992 through a detailed analysis of an extended series of sampling of CH_3Br.

The mechanism of depletion of stratosphere ozone by bromine atom has been known for a long time (Wofsy, 1975; Yung, 1980). Modeling calculations for the seasonal and vertical variations of CH_3Br mixing rate in the atmosphere has confirmed such a mechanism for CH_3Br (Singh, 1993). With the regulation of halons, which was a main bromine source in the past, the effect of CH_3Br has been predominant over the other bromine atom source. In 1998, discussion on the role of CH_3Br in the atmosphere will be an important topic in the next international atmospheric chemistry conference. Therefore, it is imperative to assess the action of CH_3Br in the atmosphere.

The reaction of OH with CH_3Br is generally through a hydrogen abstraction process, which is an exothermal one:

$$OH + CH_3Br \longrightarrow H_2O + CH_2Br.$$

The process also occurs in the troposphere when CH_3Br is transported to the stratosphere. It is a

* This study was supported by the National Natural Science Foundation of China

** To whom correspondence should be addressed

main CH_3Br removal process in the atmosphere.

We measured k'' at different temperature by using our DF-RF apparatus and calculated the lifetime and ODP (ozone depletion potential) of CH_3Br.

2 Experimental

The discharge flow technique was used with resonance fluorescence (RF) detection of OH radicals. The apparatus and the method of kinetic measurements have been described in detail earlier (Mu, 1993). A Pyrex tube with 27 mm in i.d. and 1m in length, was used as the reaction tube. An axial movable small tube 6 mm in o.d. was used as the inner tube. The wall was coated with halo-wax to reduce the wall reaction to $k_w \leqslant 18/s$. CH_3Br was carried into the reaction zone by Ar gas from the inner tube. OH radicals were produced in the reaction tube by the following fast reaction:

$$F + H_2O \longrightarrow OH + HF, \quad k = 1.16 \times 10^{-11} cm^3/(mol \cdot s) \quad (Frost, 1986).$$

F atoms were generated from CF_4 by microwave discharge (2450 MHz, 30 W) when CF_4 entered the flow tube in the side port with the carrier gas Ar. H_2O was carried into the flow tube in a downstream port. An upstream Ar flux made all kinds of gas well mixed. In the experiment, the concentration of H_2O was higher than 5×10^{14} mol/cm^3, and all of the F atoms would be transformed to HF within 10cm.

The technique of resonance fluorescence was used to detect the OH radicals. The system consisted of a resonance lamp, a detecting chamber, a monochromator, a photomultiplier, an electronic amplifier and a X-Y plane recorder. The wavelength of the monochromator was set at 309.6nm.

The reaction tube was heated by electric coils, which was controlled by two transformers. The temperature was measured with a movable semiconductor point thermometer, which could be moved out of the reaction zone during the experimental process.

The total pressure ranged from 13 to 39 Pa and the flow velocity from 600 to 1200cm/s. Our rate constant of the wall reaction was about 18/s.

The gases used had the following purity: high pure Ar $\geqslant$ 99.999% (Prex Gas), $CF_4 \geqslant$ 99.9% (Tianjin Third Nuclear Institute), $CH_3Br \geqslant$ 99.5% (Jiangsu Hormone Institute). CH_3Br has been purified by multiple colding and decolding in a vacuum. Although Argon was not further purified, passing through liquid nitrogen had been tested and no obvious change in results was observed.

3 Results and discussion

The rate constants for the reaction of OH + CH_3Br were measured at the temperature range of 288—351K. In the experiment, the concentration of OH radicals was about 10^{11}mol/cm^3, while the concentration of CH_3Br was about 10^{14}mol/cm^3. Because $[CH_3Br] \gg [OH]$, the reaction could be considered as a pseudo-first-order reaction. The kinetic equation could be written as:

$$-d[OH]/dt = k''[OH][CH_3Br] = k'[OH].$$

In the above equation, k'' is the second-order rate constant, and k' is the first-order rate constant. The relation between them is:

$$k' = k''[CH_3Br].$$

Fig. 1 shows the decay curves of OH radicals at the temperature of 307K for the reaction of $OH + CH_3Br$. Each curve corresponded to a different concentration of CH_3Br.

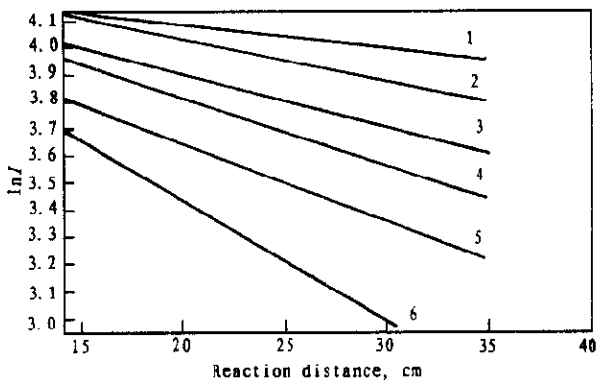

Fig. 1 The typical decay curves of OH radical signals for the reaction of $OH + CH_3Br$ at $T = 307K$

I is the fluorescence intensity of OH radicals. The concentrations (10^{-14} mol/cm^3) of CH_3Br are: 1: 2.24 2: 3.05 3: 4.37 4: 5.64 5: 7.73 6: 10.52

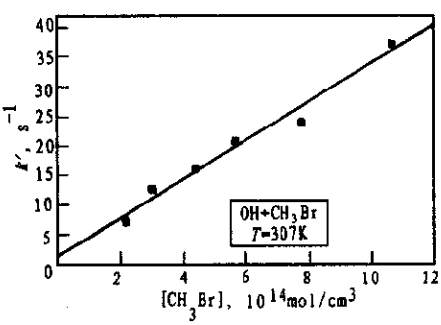

Fig. 2 The plot of the pseudo-first-order rate constant k' vs. $[CH_3Br]$ at $T = 307K$. The data are taken from Fig. 1

The value of pseudo-first-order rate constants are obtained from the decay curves of OH radicals. Fig. 2 is the plot of the pseudo-first-order constant vs. the concentration of CH_3Br at $T = 307K$. The second-order rate constant k'' is obtained from the slope of the plot of k' vs. $[CH_3Br]$ for getting the biomolecular reaction rate constant for reaction of $OH + CH_3Br$ at $T = 307K$.

The experimental conditions and kinetic constants are summarized in Table 1. The Arrhenius parameters are derived from the linear least squares fit of k'' vs. $1/T$ on natural logarithm (Fig. 3).

Table 1 Summary of experimental conditions and kinetic results

Temperature, K	$[CH_3Br]$, 10^{14}/cm^3	k'', $\times 10^{-14}$ cm^3/(mol·s)
288	3.94—12.77	2.44 ± 0.39
307	2.24—10.52	3.39 ± 0.54
320.5	6.13—15.64	3.71 ± 0.59
334.5	3.58—11.60	4.68 ± 0.75
351	4.14—16.10	6.10 ± 0.98

The errors in the determination of these parameters were calculated and described by Cvetanovic (Cvetanovic, 1979), assuming that the error in the measurement of k'' was independent on temperature. The final error of k'' is estimated to be 16%.

The derived Arrhenius expression was:

$$k'' = (3.42 \pm 0.12) \times 10^{-12}\exp(-(1419 \pm 158)/T)\text{cm}^3/(mol \cdot s).$$

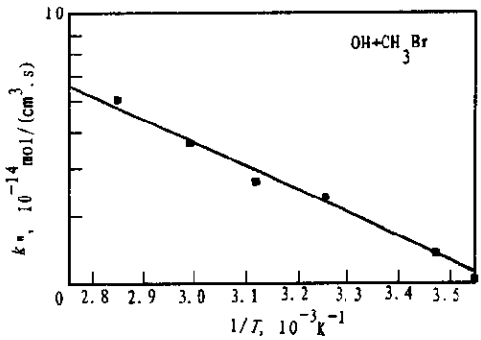

Fig.3 Arrhenius plot for the reaction $OH + CH_3Br$

Table 2 lists the comparison of our work with the previous literature data. Our k'' at $T = 298$K is in good agreement with most of the recently reported values. Our values of the activation energy and the pre-exponential factor are among the range of other results. According to our analysis, impurity should not be an important factor affecting the result. If any apparent amount of reactive impurity exist in the sample of CH_3Br, the Arrhenius plot should be somewhat curved because it should be fitted by a double-exponential function.

Table 2 Literature kinetic data for reaction $OH + CH_3Br$

$k''(298K) \times 10^{-14}$, $cm^3/(mol \cdot s)$	$A \times 10^{-12}$, $cm^3/(mol \cdot s)$	Ea/R, K	T, K	Technique*	Reference
3.5±0.8	-	-	-	DF-LMR	Howard, 1976
4.14±0.43	0.79	890±58	244—350	FP-RF	Davis, 1976
2.94±0.27	2.35	1300±150	233—379	LP-LIF	Mellouki, 1992
2.96±0.83	5.79	1560±150	250—400	FP-RF	Zhang, 1992
3.03±0.45	1.86	1230±150	248—390	DF-EPR	Chichinin, 1994
2.84±0.34	3.32	1420±160	288—351	DF-RF	This work

* DF = discharge flow; FP = flash photolysis; LP = laser photolysis; LMR = laser magnetic resonance; RF = resonance fluorescence; LIF = laser induced fluorescence; EPR = electronic paramagnetic resonance

From the result we could estimate the lifetime of CH_3Br in the troposphere. The typical average temperature is 277K in the troposphere (Prather, 1990). From the Arrhenius expression we could get the k'' value at $T = 277$K.

$$k''(277\text{K}) = 2.04 \times 10^{-14}\text{cm}^3/(\text{mol} \cdot \text{s}).$$

The average concentration of OH radicals in the troposphere is adopted as $(9.7 \pm 0.6) \times 10^5$mol/cm^3(Prinn, 1995), which corresponds to a tropospheric lifetime of 4.9 ± 0.3 years for CH_3CCl_3. So we get a value of 1.60 years for the tropospheric lifetime of CH_3Br from the following equation:

$$\tau = 1/(k[\text{OH}]).$$

The tropospheric lifetime of 1.60 years for CH_3Br is a little shorter than the previous result of 1.73 years reported by Mellouki (Mellouki, 1992), although we got nearly the same rate constant for the reaction of $OH + CH_3Br$ at $T = 277$K. The reason is that the OH concentration adopted

here is 25% higher than the previous value.

ODP (ozone depletion potential) is a measure of the integrated ozone destroying capacity over a chosen time scale of 1 kg of a particular gas emitted into the troposphere, relatively to that of a reference gas (usually CFC-11, $CFCl_3$).

We adopted a semi-empirical method to calculate the ODP value of CH_3Br. According to WMO (WMO, 1995), The semi-empirical ODP for the brominated compound X in the stratosphere may be written as the following:

$$\mathrm{ODP}_X = \left(\frac{n_X}{3} \cdot \frac{M_{\mathrm{CFC\text{-}11}}}{M_X} \cdot \frac{\tau_X}{\tau_{\mathrm{CFC\text{-}11}}} \cdot \beta\right) \cdot \left(< \frac{F_X}{F_{\mathrm{CFC\text{-}11}}} \alpha >\right)$$
$$= [\mathrm{BLP}][\mathrm{BEF}].$$

In the above equation, n_X denotes the number of bromine atom contained in a molecule of X. M_X, $M_{\mathrm{CFC\text{-}11}}$, τ_X and $\tau_{\mathrm{CFC\text{-}11}}$ denotes the molecular weight and atmospheric lifetimes of species X and CFC-11 respectively. β is the atmospheric mixing rate of X at the bottom of stratosphere to that at the ground. α denotes the rate of the efficiency of ozone depletion by bromine atom to that by chlorine atom. $F_X/F_{\mathrm{CFC\text{-}11}}$ denotes the ratio of dissociation fraction of X transported into the stratosphere to that of CFC-11. The symbol $< >$ indicates the value averaged over time and space and weighted by ozone distribution.

The term in the first parenthesis is called BLP (bromine loading potential). It denotes the rate of the number of bromine atom produced from X to the number of chlorine atom produced from CFC-11 for the same quantity of these compounds released to the atmosphere. The term in the second parenthesis present the ration of ozone depleted by bromine atoms to chlorine atoms for the same quantity of X and CFC-11.

The measurement in the stratosphere indicate $F_X/F_{\mathrm{FCF\text{-}11}} = 1.08 \pm 0.145$ for $X = CH_3Br$ (Pollack, 1992). We adopted a value of 48 for BEF of CH_3Br, which was calculated from AER 2-D Modelling (Blake, 1993). A value of 0.9 for β was selected for CH_3Br (Blake, 1993).

The atmospheric lifetime of CH_3Br and CFC-11 means a overall life time in the atmosphere. The value for CFC-11 is 50 years (Kaye, 1994). The value for CH_3Br can be calculated from the following equation:

$$\frac{1}{\tau_{CH_3Br}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{strat}} + \frac{1}{\tau_{ocean}} + \frac{1}{\tau_{other}},$$

where, τ_{CH_3Br} is the overall lifetime of CH_3Br in the atmosphere; τ_{OH} is the tropospheric lifetime of CH_3Br (1.60 years, this work); τ_{strat} is the stratospheric lifetime of CH_3Br (35 years, Prather, 1993); τ_{ocean} is the lifetime of CH_3Br determined by the ocean (Butler, 1994); τ_{other} is the lifetime determined by all the other removal processes. A value of ∞ was selected due to lack of literature value.

From the above, $\tau_{CH_3Br} = 1.08$ years is obtained. The value is shorter than the value of 1.3 years recommended by WMO in 1995. The higher concentration of OH radicals adopted here can account for such a difference.

With the above values for the parameters in the ODP expression, we can obtain ODP (CH_3Br) $= 0.33$, which is greatly lower than 0.65 reported by Mellouki (Mellouki, 1992). Besides the

difference for values of OH concentration and other parameter, they did not consider the effect of sea.

4 Conclusions

The rate constants of the reaction of CH_3Br with OH radicals have been determined by using discharge flow-resonance fluorescence method at five different temperature in the range from 288K to 351K. The derived Arrhenius equation was: $k'' = (3.42 \pm 0.12) \times 10^{-12} \exp(-(1419 \pm 158)/T) cm^3/(mol \cdot s)$. The tropospheric lifetime of CH_3Br has been estimated to be 1.60 years. An ODP value of 0.33 for methyl bromide has been obtained.

Acknowledgements——The authors thank Dr. Mu Yujing for the technical assistance.

References

Blake DR, Sive B, Zondio M, Rowland FS. EOS Trans AGU, 1993; 74(43): 134
Butler JH. Geophys Res Lett, 1994; 21:185
Chichinin A, Teton S. J Atmos Chem, 1994; 18:239
Cvetanovic RJ, Singleton DL, Paraskevopoulous G. J Chem Phys, 1979; 83:50
Divas DD, Machdo G. J Chem Phys, 1976; 65:1268
Frost RJ, Green DS. Int J Chem Kinet, 1986; 18:885
Howard CJ, Ewenson KM. J Chem Phys, 1976; 64:4303
Kaye JA, Penkett SA, Ormond FM. NASA Reference Publication No, 1339. 1994
Khalil MAK, Rasmussen RA, Gunawardena R. J Geophys Res, 1993; 98:2887
Mellouki A, Talukdar RK, Schmoltner AM, Gierczak T, Mills MJ, Solomon S, Ravishankara AR. Geophys Res Lett, 1992, 19: 2059
Mu Y, Yang W, Qiu L. Chinese J Environ Sci, 1993; 5(4):481
Pollack WH. J Geophys Res, 1992; 97:12993
Prather MJ, Spivakovsky CM. J Geophys Res, 1990; 95:18723
Prather MJ NASA/NOAA/AFEAS Workshop on atmospheric degradation of HFCs and HCFCs, Boulder, CO, 1993
Prinn RG, Science, 1995; 269:187
Singh HB, Kanakidou M. Geophys Res Lett, 1993; 5(4):481
WMO. Scientific Assessment of Ozone Depletion. 1994, 1995
Wofsy SC, McElroy MB, Yung YL. Geophys Res Lett, 1975; 2:215
Yung Y. J Atmos Sci, 1980; 37:339
Zhang Z, Saini RD. Geophys Res Lett, 1992; 12:2413

(Received July 30, 1996)