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# Kinetic and products of the $BrO + CH_3SH$ reaction: temperature and pressure dependence

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## Abstract

The kinetics and the mechanism of the reaction BrO + CH<sub>3</sub>SH  $\rightarrow$  P (1) have been studied using the mass spectrometric discharge-flow method over the temperature range 259–333 K and at low total pressure between 0.5 and 3 Torr. The temperature dependence of the reaction rate constant has been determined under pseudo-first-order kinetic conditions in excess of CH<sub>3</sub>SH over BrO radicals,  $k = (2.2 \pm 1.9) \times 10^{-15} \exp[(827 \pm 255)/T] \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. The reaction has been found to be pressure dependent in the pressure range studied. The experimental evidences suggest an addition mechanism. The studied reaction constitutes an efficient atmospheric sink for the reduced sulfur compound, CH<sub>3</sub>SH. © 2002 Published by Elsevier Science B.V.

## 1. Introduction

Gas phase sulfur compounds represent only a small fraction of the Earth's atmospheric composition, comprising less that 1 ppm by volume in air [1]. However, the chemistry of these minor constituents has a significant impact on the atmosphere and the biosphere: acid rain, visibility reduction and climate modification. An understanding of the natural sulfur cycle is thus required in order to establish a base line with which anthropogenic perturbations can be compared. Methyl mercaptan (CH<sub>3</sub>SH) is among the major trace reduced sulfur compounds emitted into the atmosphere. Natural biogenic emissions are the primary sources for this reduced compound [2]. The dominant fate of reduced sulfur compounds in the atmosphere is chemical transformation. The primary oxidants responsible for the initiation of atmospheric oxidation for CH<sub>3</sub>SH in the troposphere are the reaction with OH radicals ( $k_{298 \text{ K}} = 3.27 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [3]) and the reaction with NO<sub>3</sub> under night-time conditions ( $k = 9.21 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [3]. Under specific conditions, like in the marine boundary layer, initiation by different halogen compounds may also be important.

The principal known gas phase sources for tropospheric inorganic halogen species, including

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the oxides, are the organic halogen compounds. The oceans provide an important natural source of these compounds such as the methyl halides (CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CH<sub>3</sub>I). Once in the atmosphere, these molecules are broken down by direct photolysis or by attack by photochemically generated radicals [4]. Halogen atoms mainly react with ozone to form halogen oxides (ClO, BrO, IO). Known heterogeneous sources of halogen atoms are the reactions of sea-salt particles with nitrogen oxides and the photolysis of ozone in the presence of sea-salt particles in the ocean surface layer [5].

Several reactions of CH<sub>3</sub>SH with halogen compounds have been studied. For the reactions with F, Cl and Br, the obtained values for the rate constant at 298 K are  $2.4 \times 10^{-10}$  [6],  $1.97 \times 10^{-10}$ [7] and  $2.53 \times 10^{-12}$  [8] cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively, which are fast enough as to be considered significant in comparison with the OH and NO<sub>3</sub> reactions.

Although the total amount of chlorinated compounds is higher than species containing Br or I, the inorganic reservoirs, HOX, XONO<sub>2</sub>, HX, are rapidly photolysed when X = Br, I. So most of bromine and iodine are in their active form X or XO. In relation to the halogen oxides XO (X = I, Br and Cl), up to now, only the reaction  $CH_3SH + IO$  has been studied [9]. Halogen oxides in tropospheric air have been measured with the DOAS technique. For BrO, levels range from 5 to  $60 \times 10^8$  molecule cm<sup>-3</sup> [10] showing that their reaction towards methyl mercaptan ought to be measured in order to evaluate the potential contribution to the removal of CH<sub>3</sub>SH. So, in this work we report the first absolute kinetic study of the reaction  $BrO + CH_3SH$  (1), its temperature (259-333 K) and pressure (0.5-3 Torr) dependence, the observation of the products of reaction with the possible mechanism and its atmospheric implication.

## 2. Experimental

The kinetic experiments were carried out using the discharge flow-mass spectrometry technique (DF-MS). The experimental set-up, shown in Fig. 1, was similar to that used in previous studies in-



Fig. 1. Experimental set-up.

volving DMS and DMSO reactions with chlorine atoms [11,12]. Only details relevant to the present study are given. The main reactor consisted of a pyrex tube (100 cm length and 2.7 cm i.d.) with a jacket for the thermostated liquid circulation. A system of two injectors was used in order to sequentially generate Br atoms (injector 1) and BrO radicals (injector 2). The walls of the reactor as well as the inner surfaces of the two injectors were coated with halocarbon wax. Both radical and molecular species were sampled from the reactor and analyzed by a quadrupole mass spectrometer (VG Smart IQ<sup>+</sup>) with electron impact ion source. BrO radicals were generated in two steps. First, Br atoms were produced by passing a  $Br_2/He$  mixture through a microwave discharge and added to the He flow, inside injector 1. Secondly, BrO radicals were generated inside the movable injector 2 by reaction (2) before being introduced into the main reactor:

$$Br + O_3 \rightarrow BrO + O_2$$
 (2)

 $k_2 = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

(cf. [13]) with  $[O_3] \gg [Br]$  to ensure complete consumption of the Br atoms, in order to avoid the interference of Br + CH<sub>3</sub>SH reaction ( $k = 2.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [13]). O<sub>3</sub> was generated in an ozonizer (Ozogas, 5 g/h) and collected in a liquid N<sub>2</sub> trap before being stored diluted in helium. The O<sub>3</sub> was used freshly prepared within an experimental session to avoid the decomposition of O<sub>3</sub> in O<sub>2</sub>. Typical concentrations of Br<sub>2</sub> and O<sub>3</sub> in the reactor were (0.7–2) × 10<sup>12</sup> and (0.6–1) × 10<sup>14</sup> molecule cm<sup>-3</sup>, respectively. These chemicals were followed by mass spectrometry at m/e = 162 and m/e = 48, respectively, whereas BrO radicals was checked at m/e = 97.

The absolute concentration of BrO radicals could be measured after or before a kinetic run by titration with NO:

$$BrO + NO \rightarrow Br + NO_2$$
 (3)

$$k_3 = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(cf. [13]) with subsequent mass spectrometric quantitative detection of the NO<sub>2</sub> at m/e = 46. This NO<sub>2</sub> signal was calibrated using known NO<sub>2</sub> concentrations from a storage balloon. Typical concentration for BrO radicals was about  $5 \times 10^{11}$  molecule cm<sup>-3</sup>, excepting for experiments at T = 298 K and P = 3 Torr, where concentration was  $2 \times 10^{12}$  molecule cm<sup>-3</sup>. The detection limit for BrO was  $5 \times 10^9$  molecule cm<sup>-3</sup>. CH<sub>3</sub>SH concentrations ranged from 0.1 to  $1 \times 10^{15}$  molecule cm<sup>-3</sup>.

The purities of the gases used were as follows: O<sub>2</sub>, 99.999% (Praxair); NO,  $\geq$ 99.5% (Praxair); NO<sub>2</sub>,  $\geq$ 99.5% (Praxair); He, 99.999% (Praxair), which was passed through a liquid nitrogen trap; Br<sub>2</sub>, >99.5% (Aldrich) and CH<sub>3</sub>SH, >99.5% (Aldrich), which were purified by trap to trap distillation.

## 3. Results

The experiments were carried out within the temperature, pressure and mean flow velocity ranges (259–333) K, (0.5–3.0) Torr and (650–1400) cm s<sup>-1</sup>, respectively. In the absence of CH<sub>3</sub>SH, BrO was expected to be lost through wall heterogeneous reactions and homogeneous recombination:

$$BrO + BrO \rightarrow Br + Br + O_2$$
 (4)

 $k_4 = 5.31 \times 10^{-12} \exp(-211/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (cf. [14]) BrO + BrO  $\rightarrow$  Br<sub>2</sub> + O<sub>2</sub> (5)

 $k_5 = 1.13 \times 10^{-14} \exp(983/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (cf. [14]). Only reaction (5) involves the net elimination of BrO radicals. The formation of Br atoms in presence of an excess of O<sub>3</sub> implies the regeneration of BrO. In most cases, for the relatively low BrO concentrations used in this work, the homogeneous losses were negligible. The obtained rate constants for the wall losses were also low,  $k_w = (1-3) \text{ s}^{-1}$ . No reaction of CH<sub>3</sub>SH with Br<sub>2</sub> or O<sub>3</sub> (precursors of BrO radicals) was observed within the contact time used in the experiments (40–50 ms).

All the experimental kinetics were carried out under pseudo-first-order conditions with CH<sub>3</sub>SH in great excess over BrO with a ratio [CH<sub>3</sub>SH]/ [BrO] from 200 to 2000. The kinetic expression applying to such experiments was

$$\ln([\operatorname{BrO}]_0/[\operatorname{BrO}]_t) = (k' + k_w)t, \tag{6}$$

where  $k' = k_1[CH_3SH]$ .

Typical logarithmic decays of the intensity of BrO signal as a function of reaction time are shown in Fig. 2. A slight curvature could be conjectured for times of reaction greater than approximately 30 ms. This could be due to secondary reactions of BrO with the products of reaction (1). However this curvature could not be completely confirmed since it was not systematically observed in all the kinetic runs. Furthermore the calculated k' using times up to 30 ms generally differs in less than 5% from the calculation with times up to 50 ms and so it must not significantly affect the experimental pseudo-first-order constant. The bimolecular rate coefficient of interest,  $k_1(P, T)$ , is



Fig. 2. Examples of pseudo-first-order plots for reaction BrO + CH<sub>3</sub>SH with [CH<sub>3</sub>SH] (10<sup>14</sup> molecule cm<sup>-3</sup>) = 0.71 ( $\blacklozenge$ ), 5.34 ( $\blacksquare$ ), 8.65 ( $\blacktriangle$ ) at 298 K and P = 1 Torr. Diluent gas: He.

evaluated from the slope of k' versus [CH<sub>3</sub>SH] plot applying weighted least squares fittings. Some examples of these plots are given in Fig. 3 showing that the results are consistent with Eq. (6). In some kinetic runs at 3 Torr, the BrO concentration was slightly higher (up to  $2 \times 10^{12}$  molecule cm<sup>-3</sup>) and BrO self-recombination reaction was also taken into account using the FACSIMILE program. The values obtained in these cases for k' were from 2 to 4 s<sup>-1</sup> lower than applying Eq. (6) directly (neglecting the homogeneous recombination). The obtained results for  $k_1$  in all the experimental conditions are shown in Table 1, where errors are one standard deviation, being  $k_1(298 \text{ K}) =$  $(3.21 \pm 0.15) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Experiments were carried out at four different temperatures and 1 Torr of total pressure of helium. The reaction rate was found to increase with decreasing temperature. The data obtained are shown plotted in Arrhenius form in Fig. 4. The



Fig. 3. Second-order plot for the BrO + CH<sub>3</sub>SH reaction at different temperatures. T (K) = 259 ( $\blacksquare$ ), 298 ( $\blacklozenge$ ), 333 ( $\blacktriangle$ ) at P = 1 Torr. Diluent gas: He.

Table 1

Summary of second-order rate constants for  $BrO + CH_3SH$  reaction at different temperatures and pressures. Errors are  $\sigma$ 

T (K)	P (Torr)	$k_1$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
(K)	(1011)	(611  molecule  s)
259 278	1.0	$(5.71 \pm 0.44) \times 10^{-14}$ $(5.25 \pm 0.70) \times 10^{-14}$
298	0.5	$(5.25 \pm 0.76) \times 10^{-14}$ $(2.69 \pm 0.53) \times 10^{-14}$
	1.0	$(3.21\pm0.15) imes10^{-14}$
	3.0	$(4.85\pm0.36) imes10^{-14}$
333	1.0	$(2.93\pm0.20) imes10^{-14}$



Fig. 4. Arrhenius plot for the  $BrO + CH_3SH$  reaction at 1 Torr of total pressure in He.



Fig. 5. Rate coefficients for the  $BrO + CH_3SH$  reaction as a function of pressure. Diluent gas: He.

following Arrhenius expression, derived from that figure, was obtained:

$$k_1 = (2.2 \pm 1.9) \times 10^{-15} \\ \times \exp[(827 \pm 255)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$
(7)

Concerning the pressure range studied (from 0.5 to 3 Torr), we have found a linear pressure dependence for  $k_1$ . The rate coefficient increased when pressure was increased as it is shown in Fig. 5.

#### 4. Discussion

Reactions of  $CH_3SH$  with halogen atoms have been studied by several authors [7,8] testing the temperature and pressure dependence. For methyl mercaptan reaction with halogen oxides only the study of  $CH_3SH + IO$  reaction has been reported [9]. In that work the absolute rate constant was measured only at T = 298 K ( $k = (6.6 \pm 1.3) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) with detection of HOI as product by mass spectrometry. This Letter reports the first absolute measurement for the kinetic rate constant of reaction BrO + CH<sub>3</sub>SH and its study with temperature and pressure changes.

In this work some additional experiments increasing the concentration of the reactants were conducted to identify the products and intermediates of reaction (1). In these experiments [CH<sub>3</sub>SH] ranged from  $1 \times 10^{14}$  to  $1 \times 10^{15}$ molecule cm<sup>-3</sup> and [BrO] from  $2 \times 10^{12}$  to  $5 \times 10^{12}$ molecule  $cm^{-3}$ . The following peaks were observed by mass spectrometry, m/e = 63, 94, 96, 98, 126,128. The signals at m/e = 96, 98 are attributed to HOBr (with different isotopic Br) which is consistent with the observation of HOI as a product in the  $CH_3SH + IO$  reaction. It was verified that HOBr produced in reaction (1) did not contribute to the BrO<sup>+</sup> peak (m/e = 97) by observing a complete disappearance of the peak m/e = 97when high enough concentrations of CH<sub>3</sub>SH were used to totally consume BrO. Such a contribution of HOBr to the BrO<sup>+</sup> peak would have led to underestimate  $k_1$ . No direct calibration of HOBr could be performed and, so, the branching ratio could not be obtained.

The relative low value of the pre-exponential factor, the negative temperature dependence observed for  $k_1$ , and the increase of this constant with higher pressures clearly suggest the formation of an association complex [15,16] which can then decompose either back to reactants or to give products

$$BrO + CH_3SH \rightleftharpoons [CH_3S(OBr)H]^*$$
  

$$\rightarrow CH_3S + HOBr \qquad (1)$$

In the experiments designed to identify products, where concentrations are considerably higher than in the kinetic runs, CH<sub>3</sub>S radicals may undergo self-recombination giving DMDS (m/e = 94), reaction with Br<sub>2</sub> giving CH<sub>3</sub>SBr (m/e = 126, 128), and with ozone in excess originating CH<sub>3</sub>SO (m/e = 63), what would explain all the minor mass spectrometric peaks observed:

$$CH_3S + CH_3S \rightarrow CH_3SSCH_3$$
 (8)

$$k_{9} = 4 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}$$
  
(cf. [17])  
$$CH_{3}S + Br_{2} \rightarrow CH_{3}SBr + Br$$
(9)

$$k_{10} = (1.7 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
  
(cf. [8])  
 $CH_3S + O_3 \rightarrow P (CH_3SO)$  (10)

$$k_{11} = 5.29 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(cf. [13]).

)

The addition mechanism proposed in this work is supported by the results obtained for similar reactions. OH has been shown to react with CH<sub>3</sub>SH through the formation of a weakly bound complex [3,18]. Furthermore, DMS–BrO reaction also proceeds through the formation of a long lived addition intermediate [16].

Concerning the atmospheric implications in the removal of CH<sub>3</sub>SH by BrO, the high [BrO] tropospheric concentrations and the measured rate constant of this reaction show reaction (1) as a potentially important sink in the marine atmosphere. Although BrO-CH<sub>3</sub>SH rate constant is three orders of magnitude lower than the OH-CH<sub>3</sub>SH rate constant, the measured BrO concentration is in the range  $(5-60) \times 10^8$ molecule cm<sup>-3</sup>, much higher than the [OH] concentration  $(9.7 \times 10^5 \text{ molecule cm}^{-3} [19])$ . From the previous data, the room temperature gas phase lifetime of methyl mercaptan may be calculated as 8.7 h for OH radicals, and from 15.6 to 1.3 h for BrO. Thus, it may be concluded that CH<sub>3</sub>SH would be scavenged efficiently by BrO and so our results should be taken into account in the chemical box models to evaluate the impact of the removal of CH<sub>3</sub>SH in the marine boundary layer.

Furthermore our low pressure measurement (p < 3.0 Torr) may underestimate the real atmospheric rate constant for BrO–CH<sub>3</sub>SH since thermalization of the association complex may be inefficient. So the potential importance of reaction (1) under atmospheric conditions could even be larger and kinetic and mechanistic data are also needed.

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