



Temperature dependence of the absolute rate constant for the reaction of ozone with dimethyl sulfide

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Abstract

Absolute rate constants for the reaction of ozone with dimethyl sulfide (DMS) were measured in a 200-L Teflon chamber over the temperature range of 283–353 K. Measurements were carried out using DMS in large excess over ozone of 10 to 1 or greater. Over the indicated temperature range, the data could be fit to the simple Arrhenius expression as $k_{\text{DMS}} = (9.96 \pm 3.61) \times 10^{-11} \exp(-(7309.7 \pm 1098.2)/T) \text{ cm}^3/(\text{molecule}\cdot\text{s})$. A compared investigation of the reaction between ozone and ethene had a $k_{\text{C}_2\text{H}_4}$ value of $(1.35 \pm 0.11) \times 10^{-18} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ at room temperature.

Key words: rate constants; ozone; dimethyl sulfide (DMS); ethene

Dimethyl sulfide (DMS) is mainly produced by planktonic algae in sea water and a major source of cloud-condensation nuclei (CCN) over the oceans (Charlson *et al.*, 1987). The vast majority of DMS released into the atmosphere are removed by chemical reaction with OH (Cox and Sandalls, 1974; Kurylo, 1978; Niki *et al.*, 1983); Cl (Stickel *et al.*, 1986; Tyndall *et al.*, 1986; Nielsen *et al.*, 1990; Kinnison *et al.*, 1996) and NO_3 (Atkinson *et al.*, 1984; Tyndall *et al.*, 1986; Wallington *et al.*, 1986) radicals. Ozone is also an important oxidant in the atmosphere and responsible for consuming varieties of gas species. Only upper limit value for the reaction between DMS and O_3 at room temperature was reported in the literature (Martinez and Herron, 1978) and no temperature dependence of the rate constant of the reaction was available until now. On the basis of the only measurement for the reaction (Martinez, 1978), the NASA (National Aeronautics & Space Administration) kinetic data evaluation panel suggested an upper limit of $<1.0 \times 10^{-18} \text{ cm}^3/(\text{molecule}\cdot\text{s})$. Considering the background concentration of O_3 (40 ppbv) is approximately 10^6 times of the concentration of OH radicals, the reaction of O_3 with DMS based on the upper limit could compete with the reaction of OH with DMS. Therefore, to better understand the contribution of O_3 to the loss of DMS, the exact rate constant of the reaction is needed.

In this work, we investigated the rate constants for the reaction of ozone with DMS in the temperature range 283–353 K by using pseudo first order reaction method.

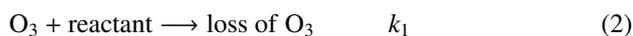
In addition, the rate constant of ethene with O_3 at room temperature was also measured to examine the reliability of our method. The atmospheric implication based on our experimental results was discussed.

The apparatus and experimental procedures have been described elsewhere (Wu *et al.*, 2003) and will only be summarized here. Briefly, the experiments were carried out in an approximately 200-L heat-sealed Teflon bag, which was hung inside a chamber (ca. 3000 L). A pair of electric fans were positioned on the opposite inner walls of the chamber ensure that a uniform temperature can be maintained during reaction of the mixture. An electrothermal strip (2.6 cm in width and 600 cm in length, 600 W, BQ 16B, Shanghai Qianwu Wiring Factory) surrounded the inner chamber for heating. In all cases, the temperature variation in the chamber was maintained to be within $\pm 1.5^\circ\text{C}$.

The required amounts of DMS and ethene were introduced into the Teflon bag by sweeping a calibrated volume contained the reactants with a stream of air. Ozone was introduced into the bag using an ozone generator (AO-12, Aijia Machine Factory, Shanghai, China). After mixing of the reactants in the bag, the ozone concentrations were monitored as a function of time by an ozone analyzer (model 8810, Monitor Labs Inc.). A gas chromatograph (GC-6AM, Shimadzu, Japan) equipped with a flame photometer detector (FPD) was used for DMS quantitative analysis. DMS in the reaction mixtures were separated on a 3 m \times 4 mm glass column packed with 20% SE 30 on Chromosorb P (60–80 mesh). The column temperature was held at 50°C . The injection port temperature and the detector temperature were 180°C and 240°C , respec-

tively. Typical gas flow rates were: nitrogen (carrier gas, 99.999%), 40 cm³/min; hydrogen, 45 cm³/min; air, 45 cm³/min. A gas chromatograph (GC4410, East & West Analytical Instrument Inc., Beijing, China) equipped with a photoionization detector (PID) was used for ethene quantitative analysis. Ethene in the reaction mixtures were separated on a 2 m × 3 mm Teflon column packed with GDX 203 (60–80 mesh) at a column temperature of 40°C.

Ozone reaction rate constants were determined by monitoring O₃ decay in the presence of known concentrations of the reactants. O₃ loss paths in the chamber can be considered as follows:



Under the experimental conditions, O₃ concentrations of (0.25–1.97) × 10¹³ molecule/cm³ were mixed with (2.5–49.8) × 10¹⁴ molecule/cm³ of reactants (DMS or ethene) in air. The concentrations of reactants were in all case 10–1000 times greater than that of O₃; hence, the observed kinetics were pseudo-first order throughout the reaction:

$$-d \ln C_{\text{O}_3} = k' dt, \quad \text{where } k' = k_0 + k_1 C_{\text{reactant}} \quad (3)$$

Thus, $-\frac{d \ln C_{\text{O}_3}}{dt}$ were determined at various reactant concentrations.

The used chemicals were ethene (≥95%, Beijing Analytical Instrument Factory, China), dimethyl sulfide (≥99.0%, Fluka). Dimethyl sulfide was further purified by repeat freeze, pump, and thaw cycles and fractional distillation before use.

The reaction between DMS and O₃ were carried out in a 200-L Teflon reaction chamber under different temperature. In all cases, exponential decays of ozone concentrations were observed. Fig.1 shows the typical plots of ln C₀(O₃) versus time under different DMS concentrations. The corresponding plots of Equation (3) are shown in Fig.2. Good straight line plots were obtained, and the pseudo-first reaction rate constants could be derived from the slopes. The error bars express in Fig.2 are two standard deviations taken from the linear least square fit of the

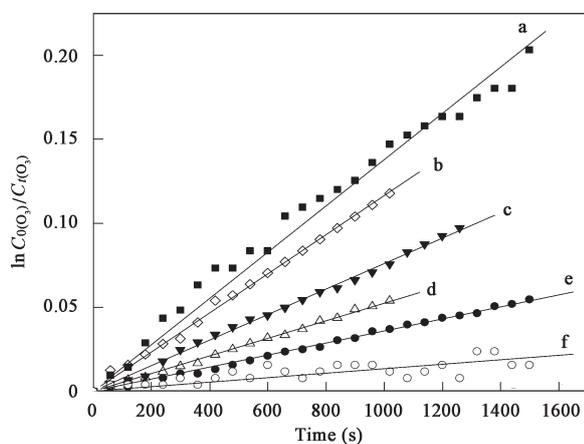


Fig. 1 Plot of $\ln C_0(\text{O}_3)/C_t(\text{O}_3)$ vs. reaction time under different concentrations of DMS at 298 K. DMS concentrations ($\times 10^{15}$ molecules/cm³): (a) 9.15; (b) 7.79; (c) 5.25; (d) 3.48; (e) 1.30 and (f) 0.

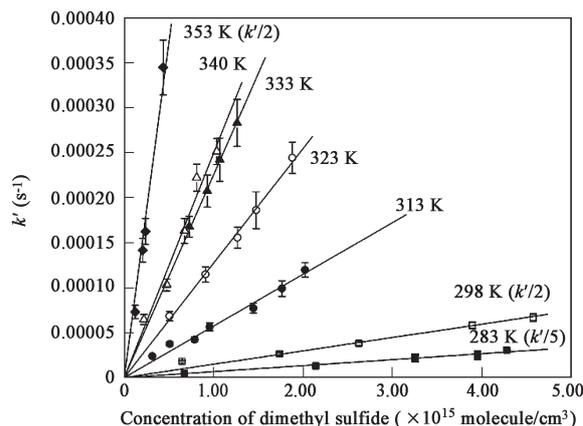


Fig. 2 Plot of the pseudo-first-order rate constant vs. concentration of DMS.

O₃ decay rate versus C_{DMS} plus an additional estimates uncertainty (5%) which was account for experimental variability due to mixture composition. These expanded error limits should, in the absence of any systematic errors, be a realistic appraisal of the 95% confidence limits.

The bimolecular rate constant of DMS at 298 K was derived as (1.48 ± 0.13) × 10⁻²⁰ cm³/(molecule·s), which is approximately 2 orders magnitude lower than the upper limit of 1.0 × 10⁻¹⁸ cm³/(molecule·s) recommended by NASA. For DMS reactions, the aerosol formation may bring secondary reactions. Simple straight line pseudo-first order rate plots can not overrule the secondary reactions. But the rate constant value of DMS at 298 K we obtained is so small that the aerosol formation can be skipped.

The Arrhenius plot is shown in Fig.3 and the Arrhenius expression in cm³/(molecule·s) over the temperature range of 283–353 K derived from the plot is: $k_{\text{DMS}} = (9.96 \pm 3.61) \times 10^{-11} \exp(-7309.7 \pm 1098.2/T)$.

Where, the error limits quoted above are one standard deviation of the fit of the points $k \pm (2\sigma + 0.05k)$ at each temperature as shown in Fig.3. It is evident that the reaction of DMS with ozone is positively dependent on temperature.

On the basis of our experimental results, the atmospheric lifetime of DMS due to O₃ attack will be about more than 2 years assuming an average O₃ concentration of 1.0 × 10¹² molecules/cm³ in the background area. Thus, the

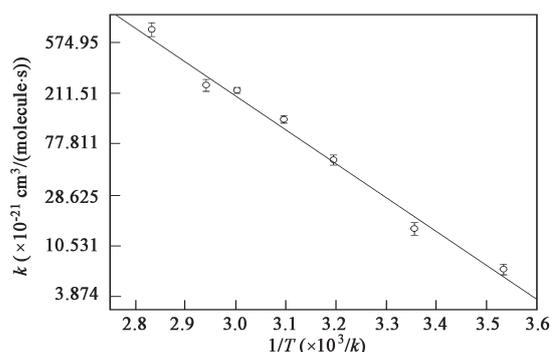


Fig. 3 Arrhenius plot for the reaction of O₃ with DMS. Each data point is based on 4–7 experiments at each temperature.

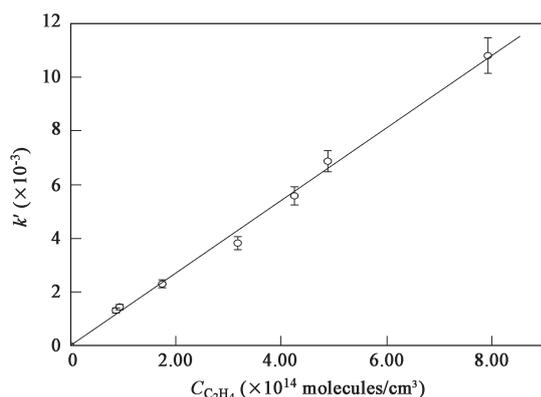


Fig. 4 Plot of the pseudo-first-order rate constant vs. the concentration of C_2H_4 .

contribution of O_3 to DMS loss in the atmosphere is only accounted for 0.2% compared with the reaction of OH ($C_{OH}: 1.0 \times 10^6 \text{ molecules/cm}^3$) with DMS, and could be negligible.

To examine the reliability of this method, the rate constant of the reaction of ethene with O_3 at room temperature (298 K) was also measured as $(1.35 \pm 0.11) \times 10^{-18} \text{ cm}^3/(\text{molecule} \cdot \text{s})$ (Fig.4) which is in good agreement with the values reported in literature (Atkinson *et al.*, 1997), providing the circumstance that the method used by this study is reliable. The calculated tropospheric lifetime of ethene with respect to O_3 is approximately 9 d at 298 K for O_3 concentrations of $1.0 \times 10^{12} \text{ molecules/cm}^3$.

As a conclusion, the reaction rate constants of the reaction between DMS and O_3 over the temperature range of 283–353 K were measured by using smog chamber technique in this study. The exact rate constants and temperature dependence for the reaction were first reported. Our results indicated that the influence of O_3 on DMS loss in the troposphere was negligible.

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