

Article ID: 1001-0742(2000)02-0189-05

Loss of ozone on sulfate and sulfide doped-ice surfaces

MU Yu-jing, ZHANG Xiao-shan, LIU Ye, YANG Wen-xiang

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

Abstract: The sticking coefficients of ozone on ice surface and solid solution of sulfate and sulfide were measured over a temperature range from 200K to 260K. Experiments were performed in a horizontal flow tube. Results indicate that the sticking coefficients of ozone on ice are in the range from 1.3×10^{-7} to 2.7×10^{-6} , and it will become larger as temperature increases; the sticking coefficients of ozone on eight kinds of 0.1 mol/L sulfate doped ice are in the range from 1.8×10^{-7} to 6.9×10^{-6} ; the sticking coefficients of ozone on four kinds of 0.1 mol/L sulfide doped ice are in the range from 3.2×10^{-7} to 2.1×10^{-5} . Ozone loss on these particles was evaluated.

Key words: sticking coefficient; ozone; ice; flow-tube; sulfate; sulfide

CLC number: X132 **Document code:** A

Introduction

Ozone plays a critical role in the earth's ecological balance owing to its strong absorption of biologically damaging incoming ultraviolet light (Susan, 1990; Sherwood, 1991). It has long been recognized that chloride can destroy stratospheric ozone, and that the emission of chlorofluorocarbons has led to a pronounced increase in the stratospheric chlorine content (Susan, 1991). However, gas phase reactions alone can not explain the phenomena such as the Antarctic "ozone hole" or ozone perturbations of the middle latitude atmosphere after volcanic eruptions (Susan, 1991; Micheal, 1994; Brasseur, 1992). It is now established that the presence of particles such as sulfate aerosol and polar stratospheric cloud (PSCs) are necessary for the occurrence of heterogeneous reactions which convert inactive reservoir species into active chlorine and also remove NO_y, thereby leading to very high concentration of ClO (Mario, 1987; Rinsland, 1994; David, 1989).

Fiocco *et al.* (Fiocco, 1989) have made lidar measurements of PSC's quasi-simultaneously with [O₃] and temperature using electrochemical-concentration-cell sounds between 12 and 18 km above South Pole, Antarctica, and found sharp minima appeared in the ozone concentration in the vicinity of PSCs. These measurements of ozone decrease in the absence of sunlight suggest the possibility of direct loss of O₃ on PSCs particles. Hofmann *et al.* (Hofmann, 1989) pointed out that there was a direct process whereby ozone molecules were destroyed following collision with particles. Because water is the major component of PSCs, it is necessary to study whether ozone exists loss on ice particles.

Edward *et al.* (Edward, 1992) have studied the sticking coefficients of ozone on ice and doped ice. The structure of their ice that was formed by filling the flow tube with solution is probably pieces of ice, can not represent the small granular ice in the PSCs. Yang *et al.* (Yang, 1996) have also studied the sticking coefficients of ozone on ice, and their results are obviously bigger than that measured by Edward *et al.* (Edward, 1992). In this paper, we report the measurements of the sticking coefficients of ozone on ice and doped ice that were determined by using flow reactor equipped with ozone detector. The ice and doped ice were formed by freezing water vapor and the aerosols of sulfate and sulfide. The ice and doped ice being formed by these methods are much more close to small granules.

1 Experiment

1.1 Experimental equipment

The loss of ozone on ice and doped ice surfaces was determined by using a tubular flow reactor equipped with ozone detector. The details of the apparatus have been discussed in our previous publications (Yang, 1996), and we will only briefly describe it in this article.

Fig. 1 is a schematic diagram of the apparatus. The flow tube was 2.2 cm in inner diameter and 68 cm in length. Thermal regulation of the reactor was achieved by circulating 95% ethanol from a special coolant bath through a jacket surrounding the flow tube. A second evacuable jacket surrounds the inner one to minimize heat loss. The temperature of the flow tube can be maintained between 200 K and 260 K. The temperature of the cooling fluid flowing through the inner jacket of the flow tube was monitored by two thermocouples at the entrance and exit of the cooling jacket. The temperature varied less than 2K during every experiment and the difference of the temperatures between entrance and exit was no more than 2K. The pressure of the system was monitored with a capacitance manometer located at the bottom of the flow tube. In this work, the flow tube was operated at pressures between 59 KPa and 95 KPa.

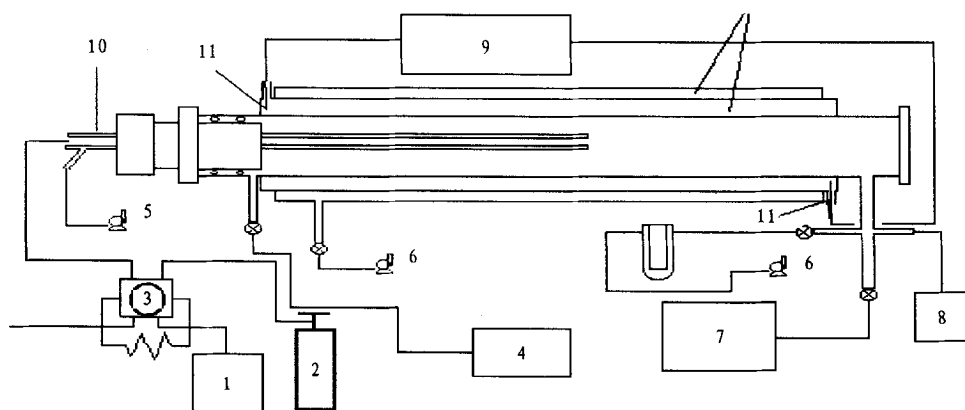


Fig. 1 Schematic diagram of the experimental apparatus

1. ozone generator; 2. carrier gas; 3. six port valve; 4. aerosol generator; 5. air compressor; 6. pump; 7. ozone detector (ozone analyzer, model 8410); 8. manometer; 9. coolant; 10. movable injector; 11. thermocouple; 12. jacket

A movable injector consisting of a jacketed glass tube with an inner diameter of 0.25 cm and an outer diameter of 1.1 cm, was heated by passing dry air at room temperature through its jacket in order to prevent condensation within the injector. Ozone was pulsingly introduced into reactor tube through 6-valve. The reaction time was determined by the position of the injector. Part of the reactant gases passed to ozone detector (Monitor labs, ozone analyzer, model 8410) through a branch tube. The detection limit for O_3 was approximately 1×10^{11} mol/cm³. Most of experiments were carried out with an initial ozone concentration of approximately $5-10 \times 10^{12}$ mol/cm³. Argon (99.999%) was selected as carrier gas.

1.2 Ice surface

The ice surface was prepared by high purity nitrogen blowing bubbles through deionization water reservoir to the reactor which had been cooled to a given temperature. The pressure in the reactor was less than 25 kPa during the coating procedure.

Sulfate and sulfide doped ice surfaces were prepared by freezing the aerosols generated by a

vibrating orifice aerosol generator(tsi. model 3450).

The amount of deposited ice substrate were calculated from the weight of the ices which were transferred to a trap at 77K. Average film thickness was calculated by using the measured geometric area and weight of the deposit ice, and the results ranged from 16 μm to 37 μm . The ice surface area was considered as geometric surface area.

There is a window at the bottom of reactor through which the ice surface can be observed. In the temperature range of 200—260K, a thin layer of white frostily solid could be seen. The ice surface was not very uniform, the layer was usually thinner at top than at bottom of the tube, and thicker in the forth than in the rear.

1.3 Experimental principle

The loss of ozone on ice or doped ice surfaces was considered as pseudo-first order reaction. If K_s was the first reaction rate constant of ozone loss in ice or doped ice, and N was the total number of ozone molecules introducing into the reactor, then NK_s (mol/s) was the molecules of ozone losing on the ice surface per second. The sticking coefficient(γ) was defined as follows(Brasseur, 1992):

$$\gamma = \frac{\text{number of reactant molecules lost (mol/s)}}{\text{number of gas-surface collisions (Colli./s)}}$$

The total gas-surface collision frequency, Z (colli./s) is obtained from kinetic theory as:

$$Z = \frac{1}{4} \times \omega \times A_s \times \frac{N}{V},$$

where ω is the average molecular velocity(cm/s), A_s is the area of the surface (cm^2), and N/V is the number of reactant gas per cm^3 .

The expression of sticking coefficient can be easily obtained as follows:

$$\gamma = \frac{2K_s \cdot r}{\omega}$$

Where r is the radius of the flow tube after accounting for the ice surface thickness(cm).

1.4 Reagents

| | | | |
|---------------------------------------------------------------------|-------|---------------------------------------------------------|-------|
| $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ | A. R. | $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ | A. R. |
| $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ | A. R. | $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | A. R. |
| NaHSO_3 | A. R. | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | A. R. |
| $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ | A. R. | K_2SO_3 | C. R. |
| K_2SO_4 | A. R. | $(\text{NH}_4)_2\text{SO}_4$ | A. R. |
| $(\text{NH}_4)_2\text{SO}_3$ | C. R. | Na_2SO_3 | A. R. |

2 Results and discussion

The loss of ozone on ice and doped ice is considered as a pseudo-first order reaction, the following equation holds for the decay of ozone:

$$\log C(x) = -K_s(x/v) + \log C(0).$$

Where C is the ozone concentration signal, 0 is the reference injector position, v is the average flow velocity, and x is the injector position. $\log C(x)$ were plotted versus the injector position, a straight line can be given and the reaction rate constants K_s were obtained from the linear least-squares fit to these data. Fig. 2 shows a typical example of ozone loss on bare tube, ice and doped ices. When ozone exposed

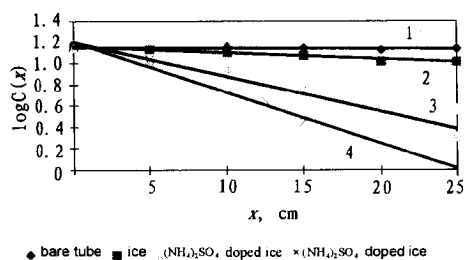


Fig. 2 $\log C(x)$ versus the injector position

on bare tube the signal of ozone was independent of the injector position. But the loss of ozone on ice and doped ice was obvious.

The sticking coefficients can be determined by the equation:

$$\gamma = 2K_s r / \omega.$$

Table 1 The sticking coefficients for O₃ on ice

| T, K | K _s /s | γ | T, K | K _s /s | γ |
|-----------|-------------------|---------|------|-------------------|---------|
| 201 | 3.2E-02 | 2.4E-07 | 238 | 2.0E-02 | 1.4E-06 |
| 211 | 5.6E-03 | 4.0E-07 | 252 | 4.2E-02 | 2.7E-06 |
| 221 | 1.8E-03 | 1.3E-07 | 245 | 9.3E-03 | 6.2E-07 |
| 223 | 1.1E-02 | 7.5E-07 | 259 | 3.2E-02 | 2.1E-06 |
| 226 | 5.9E-03 | 4.1E-07 | 261 | 1.9E-02 | 1.2E-06 |
| 227 | 2.0E-02 | 1.3E-06 | | | |
| Bare tube | | | | | |
| 242 | 9.9E-04 | 6.6E-08 | 242 | 1.2E-03 | 8.2E-08 |

as temperature increasing; the sticking coefficient at 199K can be calculated as $\gamma = 1.2 \times 10^{-7}$. It is very closed to the result of Edward *et al.* ($\gamma = 2.5 \times 10^{-7}$; Edward, 1992).

The sticking coefficients of ozone on the surfaces of sulfate and sulfide doped ice are listed in Table 2. The sticking coefficients of ozone on sulfate and sulfide doped ice are larger than that of ozone on ice except on K₂SO₄, FeSO₄(NH₄)₂SO₄·6H₂O and NaHSO₃ doped ice. Especially the sticking coefficients of ozone on (NH₄)₂SO₄·H₂O, MnSO₄·H₂O and some sulfide doped ice are significant larger than that of ozone on ice. The large sticking coefficients of ozone on these compounds doped ice may be ascribed to the oxidation of NH₄⁺, Mn²⁺ and SO₃²⁻ by ozone. However, the sticking coefficient of ozone on NaHSO₃ doped ice is less than that of ozone on ice. If we considered the loss of ozone on NaHSO₃ doped ice as chemical loss, there maybe exists a higher energy barrier for oxidation of HSO₃⁻ than that of SO₃²⁻. Previous work on the measurement of oxidation of SO₂ solution suggested (Penkett, 1986) that the oxidation almost ceased when SO₃²⁻ was consumed completely, and HSO₃⁻ remained only. This may be the circumstantial evidence for the less sticking coefficient of ozone on NaHSO₃ doped ice. The less or larger sticking coefficients of ozone on doped ice than that of ozone on ice may be caused by different crystal being formed at low temperature; some were feasible to ozone loss, others on the contrary.

Edward *et al.* (Edward, 1992) have measured the sticking coefficients of ozone on 0.1 mol/L Na₂SO₃ doped ice at 196K. Their results are 3—5 orders of magnitude larger than ours. Edward *et al.* (Edward, 1992) pointed out the dependence of γ on ozone concentration was caused by saturation effects. The concentration of ozone in our experiments is 2 orders of magnitude higher than that of Edward *et al.* (Edward, 1992), so it is not surprising that our results is lower than theirs. According to the results of Edward *et al.* (Edward, 1992), we can easily estimate ozone molecule number lost on a fixed area of Na₂SO₃ doped ice, such as 5 cm of Na₂SO₃ doped ice, and assume the flow velocity is 1280 cm/s, the number of ozone lost on their doped ice is 6.2×10^7 — 1.3×10^9 molecules. Under our experimental condition, the number of ozone lost on the doped ice is approximately in the range from 8×10^9 to 1.5×10^{11} molecules, is about two orders of

The sticking coefficients of O₃ on ice and bare tube are summarized in Table 1. It is obvious that the data of sticking coefficients are disperse with temperature. Fig. 3 is the plot $\log \gamma$ against $1/T$. The correlation coefficient is about 0.7, and the results can be expressed in the following equation.

$$\log \gamma = - (1021/T) - 1.77.$$

Although the correlation between the sticking coefficients and temperature is not very good, in general, γ will become large

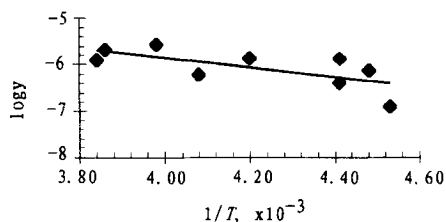


Fig. 3 The plot of $\log \gamma$ against $1/T$

magnitude more than theirs. This may be caused by higher temperature in our experiments than that of Edward *et al.* (Edward, 1992). In addition, the crystal structure may have some effects. Edward *et al.* (Edward, 1992) formed the doped ice by filling the flow tube with solution, and the doped ice is probably pieces of ice; whereas our doped ice was formed by freezing the aerosols for sulfide, the doped ice is close to small granules.

Table 2 The sticking coefficients of ozone on the surfaces of 0.1 mol/L sulfate and sulfide doped ice

| 0.1mol/L sulfate | T, K | K_s/s , $\times 10^{-3}$ | γ , $\times 10^{-7}$ | γ_{ice} , $\times 10^{-7}$ | 0.1mol/L, sulfide | T, K | K_s/s , $\times 10^{-3}$ | γ , $\times 10^{-7}$ | γ_{ice} , $\times 10^{-7}$ |
|-----------------------------------------|------|-------------------------------|--------------------------------|--------------------------------------|-------------------|------|-------------------------------|--------------------------------|--------------------------------------|
| $Na_2SO_4 \cdot 10H_2O$ | 233 | 21.8 | 14.8 | 6.8 | Na_2SO_3 | 238 | 51.4 | 46 | 8.8 |
| $MgSO_4 \cdot 7H_2O$ | 257 | 42.5 | 27.6 | 18.5 | | 220 | 10.5 | 9.3 | 3.9 |
| K_2SO_4 | 231 | 4.82 | 3.3 | 6.5 | K_2SO_3 | 238 | 42.9 | 38 | 8.8 |
| $Al_2(SO_4)_3 \cdot 18H_2O$ | 246 | 33.6 | 22.3 | 12.1 | — | — | — | — | — |
| $(NH_4)_2SO_4$ | 256 | 107 | 69 | 17.5 | $(NH_4)_2SO_3$ | 238 | 232 | 210 | 8.8 |
| $MnSO_4 \cdot H_2O$ | 235 | 58.8 | 39.9 | 7.7 | | 222 | 14.4 | 13 | 4.3 |
| $FeSO_4(NH_4)_2 \cdot SO_4 \cdot 6H_2O$ | 250 | 2.72 | 1.79 | 14.1 | $NaHSO_3$ | 239 | 3.65 | 3.2 | 9.1 |
| $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ | 233 | 21.8 | 14.8 | 6.8 | | 227 | 0.55 | 0.49 | 5.4 |

Notes: γ_{ice} was calculated from the equation, $\log \gamma = -(1021/T) - 1.77$

Atmosphere implication: The loss of ozone on ice surface can be considered as first order reaction, the lifetime of ozone for deposition on the ice surface may be taken as $\tau = 4/(\omega\gamma A)$, here ω the average molecular velocity, γ the sticking coefficient, A the surface area available. Edward *et al.* (Edward, 1992) using their upper limit (10^{-6}), and assuming a surface area of $10^{-5} \text{ cm}^2/\text{cm}^3$ (type III PSCs), estimated the life time of ozone was 150 days, and therefore they pointed out ozone loss on particle surface composed mainly of water is negligible. Under the same condition, using our upper limit (2.7×10^{-6}), the life time of ozone is only 56 days. Because the concentration of ozone we used is much higher than that of stratosphere, our results can only represent the lower limits for ozone loss on ice. Under the condition of stratosphere, the loss of ozone on ice maybe more significant. So, ozone loss on particle surface composed mainly of water can not be ignored.

References:

- Brasseur G, Granier C, 1992. Science[J], 257:1239—1242.
 David J H, 1989. J Geophys Res[J], 94(D4):5029—5041.
 Edward J D, 1992. Geophys Res Lett[J], 19(1):41—44.
 Fiocco G, 1989. Nature[J], 341:426—427.
 Hofmann D J, 1989. Nature[J], 337:447—449.
 Micheal Y D, 1994. J Geophys Res[J], 99(D12):25681—25696.
 Mario J M, 1987. Science[J], 238:1253—1257.
 Penkett S A, 1986. Chemistry of Multiphase Atmospheric Systems[J], 507—540.
 Rinsland C P, 1994. J Geophys Res[J], 99(D4):8213—8219.
 Susan Solomon, 1990. Nature[J], 347:347—354.
 Sherwood F, Rowland, 1991. Annu Rev Phys Chem[J], 42:731—768.
 Yang W X, Mu Y J, Liu Y, 1996. Chinese Science Bulletin[J], 41(4):343—345.