

Article ID: 1001-0742(2000)02-0194-05

Reaction probabilities of ClONO₂ on ice

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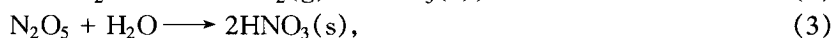
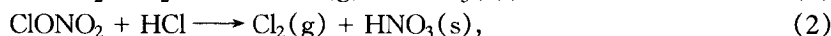
Abstract: The reaction probabilities of ClONO₂ on ice surface were determined by using a flow tube reactor attached with a photoionization detector. The growth rate of HOCl was used to obtain reaction probabilities. The measured reaction probabilities depended on temperature and flow velocity. The reaction proceeded efficiently at temperature range of 190K to 200K. The reaction probability was 0.0023 at 198K ($v = 100$ cm/s). The result was in good agreement with that of Abbatt *et al.*

Key words: reaction probability; PSCs; ClONO₂; ozone hole

CLC number: X515 **Document code:** A

Introduction

The ozone hole has become a seasonal phenomenon in south polar since the discovery of Antarctic ozone hole in 1985 (Farman, 1985). The ozone hole formation needs a great number of active chlorine atoms (such as Cl and ClO) and lower concentration of NO₂. However, the gas phase reaction alone cannot produce the active chlorine levels necessary to explain the observed ozone decrease. It is established well that stratospheric ozone depletion in the polar regions is largely due to the heterogeneous processes occurring on the surfaces of polar stratospheric clouds (PSCs). The heterogeneous reactions of primary interest in the polar stratosphere are as follows (Leu, 1991; Hanson, 1991; Zhang, 1994):



The HOCl, Cl₂ and ClNO₂ produced in these reactions are readily photodissociated in the polar springtime releasing active chlorine which can destroy ozone. The formation of HNO₃ can effectively remove gas-phase reactive nitrogen radicals (NO_x) which can react with halogen radicals to form relatively stable reservoir species, so that it is also crucial to the efficiency of ozone destruction (Hanson, 1991).

Two main types of PSCs can be formed for the chemical composition and temperature observed in the Antarctic stratosphere during winter and spring (WMO, 1994): type I particles are nitric acid trihydrate (NAT) and form at a temperature of ~197K; type II particles form at frost point (~187K) and are mainly water. There have been several experimental kinetic studies of reactions (1)–(4) on the two types of PSCs, and the reaction probabilities (γ 's) have been measured on water ice and NAT (Leu, 1991; Hanson, 1991; Zhang, 1994). The results indicated that reaction (1) and (2) can occur readily on surfaces of water ice and NAT. However, a wide range of measured γ_1 has been reported, ranging from 0.002 to ≥ 0.3 (Abbatt, 1992; Hanson, 1991) in the literature. This discrepancy was considered as due to the difference in ClONO₂ partial pressures used in each of those studies; high ClONO₂ partial pressures lead to surface saturation by HNO₃ of reaction (1) and caused deactivation of the ice surface. However, under the same level of ClONO₂ partial pressure, the reaction probability measured by Zhang *et al.* is 0.08 ± 0.02 (Zhang, 1994), it is smaller than that reported by Hanson and Revishankara (0.3) (Hanson,

1991).

In this paper, we report the investigation of reaction (1) on the ice surface by using a photoionization detector, and compare our results with previous measurements.

1 Experiment

The apparatus and experimental procedures are essentially the same as those used in our previous studies (Yang, 1996). The following is brief description of the experiment.

The reaction probabilities of ClONO₂ on ice was studied in a horizontally-mounted cylindrical flow tube with an inner diameter of 2.2 cm (Fig. 1). Its inner wall was covered with ice formed by freezing droplet of deionization water generated by aerosol generator (tsi, Model 3450). The thickness of the ice film is about 17–36 μm. The flow tube was operated at pressures from 9.1 kPa to 15 kPa and carrier gas flow velocities from 0.7 to 100 cm/s. The substrate temperature was considered as that of coolant, and maintained between 187K and 232K.

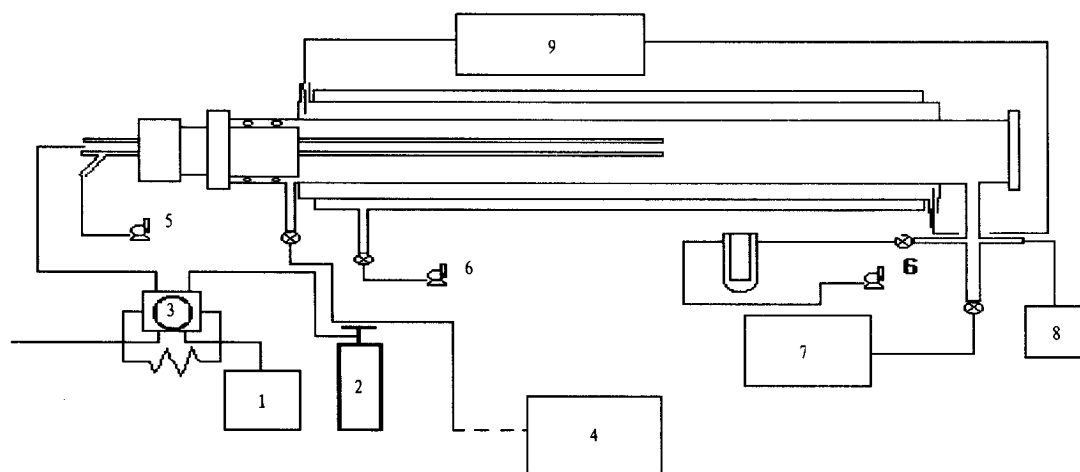


Fig.1 Schematic diagram of the experimental apparatus

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

ClONO₂ was prepared by the following procedures: (1) synthesis of Cl₂O (Davidson, 1987): it is synthesized by dry Cl₂ and air passing through HgO maintained at 18–20°C. (2) synthesis of N₂O₅ (Davidson, 1987; Schack, 1967): it is synthesized by the reaction of HNO₃ with P₂O₅, and distilled by oxygen containing ozone. (3) synthesis of ClONO₂ (Davidson, 1987; Schack, 1967): it was prepared by the method of mixing Cl₂O and excess of N₂O₅ at 196K in the dark and was further distilled from 196K to 77K.

ClONO₂ was diluted by N₂ flowing through a ClONO₂ bubbler maintained at 195K (in dry ice bath). The diluted sample was continually passing through a quantitative tube which connected with a 6-valve, and injected into the reactor by pulsing way. The gases exited from the reactor were divided into two parts, one part directly connected to photoionization detector by passing through teflon tube. The other part and the exited gases from the detector connected a pump. The concentration of ClONO₂ in the gas stream exiting the bubbler was calculated by assuming that the gas mixture was ideal and that N₂ was saturated with ClONO₂ at its vapor pressure of about 1.2 torr, which was measured by Leu *et al.* (Leu, 1991).

Photoionization detector (PID-100C, made by Institute of RCEES) consists of a discharge lamp without electrode, and can emit about 120 nm ultraviolet light. It can detect the gas compounds whose ionization potentials are lower than 10.6 eV. However, although the ionization

potentials of some compounds exceed 10.6 eV, such as Freon 11, 12, 13 and some chlorine compounds, the detector can also detect them with high sensitivity.

2 Results and discussion

The reaction of ClONO₂ on ice was considered as irreversible first-order reaction, hence the following equation holds for the reactant:

$$\log[S_t(z)] = -K_s(z/v) + \log[S_t(0)], \quad (5)$$

where S_t is the signal, 0 is the reference injector position, v is the average flow velocity, and z is the injector position. The corresponding equation for the product signal, assuming rapid desorption and unit stoichiometry, is given by

$$\log[S_t(\infty) - S_t(z)] = -K_s(z/v) + \log[S_t(\infty) - S_t(0)], \quad (6)$$

where $S_t(\infty)$ is the signal when the reaction has reached completion. Because photoionization detector can not distinguish the reactant and products, we just consider the increase of signal as that of products.

The left-hand side of Equation (6) were plotted vs injector position for product formation. The reaction rate constants K_s were obtained from linear least-squares fit to these data.

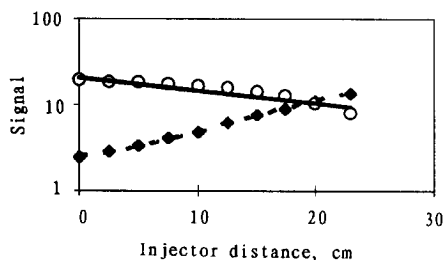


Fig. 2 Dashed line: HOCl signal as a function of injector position

Solid line: $S_t(\infty) - S_t(z)$ ($T = 198\text{K}$, $P = 9.7\text{kPa}$, $v = 100\text{ cm/s}$, $\gamma = 0.0023$)

Fig. 2 shows a typical example of signal vs reaction distance for reaction (1). The reaction probability (γ) can be obtained according to the following equation:

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

Where γ is the radius of the flow tube after accounting for the ice surface thickness (cm), ω is the average molecular velocity (cm/s).

The reaction probabilities of ClONO₂ on ice under different conditions are summarized in Table 1. The results indicated that the reaction probabilities strongly dependent on flow velocity and temperature, whereas pressure and the concentration of ClONO₂

Table 1 The reaction probability of ClONO₂ on ice

P , kPa	v , cm/s	T , K	C , mol/cm ³	γ , $\times 10^{-4}$	P , kPa	v , cm/s	T , K	C , mol/cm ³	γ , $\times 10^{-4}$
13.3	0.7	205	9.4×10^{14}	0.13	10.3	33.3	205	7.8×10^{14}	5.8
13.3	0.7	205	9.4×10^{14}	0.11	10.3	33.3	205	7.8×10^{14}	3.6
7.9	4.1	187	6.5×10^{14}	1.5	10.8	33.3	205	8.0×10^{14}	3.2
9.8	10.0	200	7.8×10^{14}	1.4	9.8	33.3	216	7.7×10^{14}	1.2
9.8	10.0	200	7.8×10^{14}	2.0	9.8	33.3	221	6.9×10^{14}	1.6*
10.0	10.0	191	8.1×10^{14}	2.1	9.8	42.0	226	7.4×10^{14}	0.2*
7.9	10.0	189	6.4×10^{14}	2.2	9.8	50.0	207	7.4×10^{14}	9.3
9.8	15.0	207	7.4×10^{14}	2.6	10.1	100.0	204	7.7×10^{14}	14.8
11.4	16.7	205	8.8×10^{14}	1.9	10.1	100.0	190	8.3×10^{14}	21.1
11.4	16.7	205	8.8×10^{14}	1.6	9.7	100.0	188	8.1×10^{14}	14.8
10.8	17.0	232	7.2×10^{14}	1.5*	9.7	100.0	198	7.7×10^{14}	22.9
10.5	22.5	215	7.6×10^{14}	4.1	9.7	100.0	201	7.4×10^{14}	19.1
10.8	33.0	206	8.1×10^{14}	4.2	9.7	100.0	200	7.5×10^{14}	22.1
9.8	33.0	210	7.3×10^{14}	2.5	9.7	100.0	202	7.2×10^{14}	18.0
Bare tube									
9.8	33.0	220	7.1×10^{14}	0.057*	10.2	10.0	293	2.3×10^{15}	0.073*
11.0	16.7	215	8.3×10^{14}	0.085*	9.8	8.4	291	1.8×10^{15}	0.067*

* the signal of photoionization detector decreases as injector position increases

had no obvious impact on the reaction probabilities under the experimental conditions. The signal of photoionization detector decreases as injector distance increases when the temperature is higher than 220K or when ClONO₂ expose on bare tube. If the reaction takes place, this indicates that the reaction may be very slow or the product (HOCl) retained on the ice surface under higher temperature. If no reaction happens, the decrease of the signal ascribe to the physical absorption of ClONO₂ on ice.

2.1 The impact of temperature on measured reaction probability

To demonstrate the effect of temperature on the reaction probability, a set of experiments were conducted on ice films over a range of temperatures under a typical flow rate (100 cm/s). The results are depicted in Fig. 3. At high temperatures ($T > 205\text{K}$), the reaction probability is observed to be less than 10^{-3} , whereas it increases substantially when temperatures become low ($\gamma > 10^{-3}$), and it decreases again when temperature lower than 190K. Almost same conclusion was drawn by Zhang *et al.* (Zhang, 1994) when they studied hydrolysis of ClONO₂ on H₂SO₄ · 4H₂O doped ice surfaces. It should be noted that the discrepancy for our measured reaction probability is about $-36\% \sim +57\%$ at flow rate of 100 cm/s and temperature of 200K. The large discrepancy of our results may be cause by unstable water vapor in the reactor (Zhang, 1994).

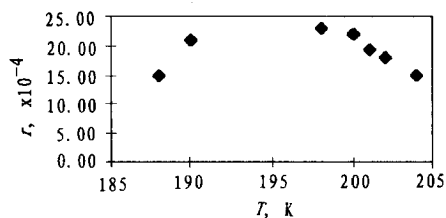


Fig. 3 Reaction probability as a function of temperature ($v = 100 \text{ cm/s}$)

2.2 The impact of flow velocity on measured reaction probability

The reaction probability is defined as the ratio of the number of molecules reacting on the surface to the number of molecules colliding with the surface at steady state. The number of molecules reacting on the surface is determined by the number of available surface sites and the number of molecules colliding with the surface. Because the ice surface can be contaminated by the product (HNO₃) for reaction (1) (Hanson, 1991), the number of available surface sites is determined by the quantity of HNO₃ formation. For a fixed reaction ice surface, the number of reactants collision with the ice surface for fast flow velocity is relative less to slow flow velocity, whereas the ratio of the number of available surface sites to the number of reactants collision is relative higher for fast flow velocity than slow velocity. If concentrations of reactants were high, the flow velocity will have more important influence on the measured reaction probability because of contamination. It is estimated that approximately 2×10^{14} molecules cm^{-2} of ClONO₂ deposited on the surfaces of ice particles would produce a monolayer of NAT. The concentration of ClONO₂ is about $(6.4\text{--}9.4) \times 10^{14}$ molecules cm^{-3} in our experiments, is much higher than that of a monolayer of NAT formation. The impact of flow velocity on our measured reaction probability is significant. Fig. 4 shows the relationship between the flow velocity and measured reaction probability.

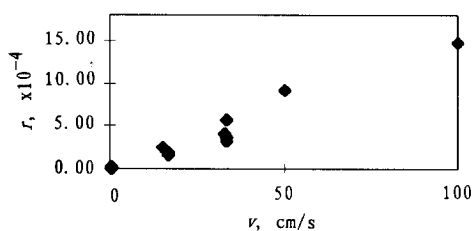


Fig. 4 The impact of flow velocity on measured reaction probability ($P = 9.5\text{--}11.7 \text{ kPa}$, $T = 204\text{--}207\text{K}$)

There are no report about the impact of flow velocity on measured reaction probability in the literature, but the experimental data of Leu *et al.* (Leu, 1991) indicate the flow velocity have some impact of measured reaction probability.

2.3 Comparison of measured reaction probabilities

The previous measurements of the reaction probabilities for ClONO₂ on ice surface are summarized in Table 2. A wide variation of γ_1 measurements on the ice surfaces could be seen. The differences of the results from different laboratories

were ascribed to the different concentrations of ClONO₂ were employed. However, even if same level concentration of ClONO₂ was used, the differences of the results from different laboratories are very large. So, in addition to the effect of concentration of reactants on measured reaction probabilities, the impact of temperature and flow velocity must be considered. As mentioned above, the ice surface can be easily contaminated by the product (HOCl) of reaction (1), and a monolayer of NAT can be easily formed when high concentration of ClONO₂ was employed. Therefore the reaction probabilities measured by using high concentration of ClONO₂ are similar to the reaction probabilities of ClONO₂ on NAT surface (except the results of Molina *et al.*, 1987). Any way, the results measured by different laboratories were instrumental in showing that reaction (1) are important in the polar stratosphere.

Table 2 Comparison of measured reaction probabilities

Velocity, cm/s	1100—20000	1000	1300—3000	1300—3000	500—2000	500—2000		1760	100
T, K	195	200	200—202	200—202	202	202	185	196	198
Concentration × 10 ¹²	0.001—0.005	100—480	0.004—0.07	0.004—0.07	>0.3	0.01—0.1	4	2.3	770
γ	0.08 ± 0.02	0.02	≥0.3	0.006	0.002	0.002	0.009	0.0017	0.0023
Substrate	ice	ice	ice	NAT	ice	NAT	ice	MAT	ice
Investigator	Zhang, 1994	Molina, 1987	Hanson, 1991		Abbatt, 1992		Tolbert, 1987	Leu, 1991	This work

The unit of concentration is molecule/cm³

3 Conclusion

The principal conclusion from this work is that the temperature and flow velocity have a strong influence on measured reaction probabilities of reaction (1). The reaction proceed efficiently at temperature range from 200K to 190K. The influence of velocity on measured reaction probability is mainly caused by contamination of the product (HNO₃) for reaction (1). Reaction (1) is important for polar stratospheric ozone depletion.

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(Received for review September 23, 1998. Accepted October 28, 1998)