Reports

Reaction of Chlorine Nitrate with Hydrogen Chloride and Water at Antarctic Stratospheric Temperatures

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Laboratory studies of heterogeneous reactions important for ozone depletion over Antarctica are reported. The reaction of chlorine nitrate ($ClONO_2$) with H_2O and hydrogen chloride (HCl) on surfaces that simulate polar stratospheric clouds [ice and nitric acid (HNO_3)–ice and sulfuric acid] are studied at temperatures relevant to the Antarctic stratosphere. The reaction of $ClONO_2$ on ice and certain mixtures of HNO_3 and ice proceeded readily. The sticking coefficient of $ClONO_2$ on ice of 0.009 ± 0.002 was observed. A reaction produced gas-phase hypochlorous acid (HOCl) and condensed-phase HNO_3; HOCl underwent a secondary reaction on ice producing dichlorine monoxide (Cl_2O). In addition to the reaction with H_2O, $ClONO_2$ reacted with HCl on ice to form gas-phase chlorine (Cl_2) and condensed-phase HNO_3. Essentially all of the HCl in the bulk of the ice can react with $ClONO_2$ on the ice surface. The gaseous products of the above reactions, HOCl, Cl_2O, and Cl_2, could readily photolyze in the Antarctic spring to produce active chlorine for ozone depletion. Furthermore, the formation of condensed-phase HNO_3 could serve as a sink for odd nitrogen species that would otherwise scavenge the active chlorine.

SEVERAL MECHANISMS HAVE BEEN proposed to explain the dramatic reduction of ozone levels observed in the spring over Antarctica (*1–7*). Chemical mechanisms for ozone destruction generally rely on the presence of active chlorine [atomic chlorine (Cl) and chlorine monoxide (ClO)] in the stratosphere (*2–5*). However, homogeneous reactions alone cannot produce the active chlorine levels necessary to explain the observed ozone decrease (*3*). The source of active chlorine may be heterogeneous reactions that occur on the surface of so-called polar stratospheric clouds (PSCs) over Antarctica (*3*). For example, reactions 1 and 2:

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \quad (1)$$

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \quad (2)$$

may be catalyzed at low temperatures on PSCs (*3*); these reactions convert inert chlorine reservoir species [chlorine nitrate ($ClONO_2$) and hydrogen chloride (HCl)] into more active forms of chlorine [hypochlorous acid (HOCl) and chlorine (Cl_2)], which photolyze readily in the Antarctic spring.

Although the composition of the PSCs over Antarctica is unknown, PSCs are thought to consist mainly of frozen mixtures of nitric acid (HNO_3) and water (*6, 7*). Other aerosols that contain sulfuric acid (H_2SO_4) may also be important in the heterogeneous chemistry of the Antarctic stratosphere (*8*). Previous work in our laboratory has shown that at room temperature, H_2SO_4 is an effective catalyst for reaction 1 (*9*). We report the reactions of $ClONO_2$ on surfaces that simulate PSCs (ice and nitric acid–ice and sulfuric acid) at temperatures relevant to the Antarctic stratosphere (185 to 208 K) and the reaction of $ClONO_2$ with HCl on cold surfaces.

Reactions 1 and 2 were studied with a modified version of a Knudsen cell flow reactor (*10, 11*). The Knudsen cell consists of two chambers, one of which contains the cold surface of interest. The chambers are separated by a sliding glass seal that can be opened to expose the cold surface to the reactants. The gas-phase contents of the Knudsen cell are sampled with a mass spectrometer. Changes in mass spectrometer signals when the glass seal is opened reflect reactions that occur on the cold surface. Reaction products that remain on the cold surface are detected subsequently with thermal desorption spectrometry (TDS), in which the partial pressures of the products are monitored as the temperature of the surface is slowly increased. Synthesis of $ClONO_2$ is described in (*9*).

Reaction 1 occurred readily on ice and on certain nitric acid–ice mixtures at 185 K. The reaction was monitored by the disappearance of $ClONO_2$ and the formation of both HOCl and HNO_3

Typical mass scans of the Knudsen cell effluent for the reaction of $ClONO_2$ on ice at 185 K are shown in Fig. 1. The mass spectrum of $ClONO_2$ in the presence of water before exposure to ice shows the characteristic $ClONO_2$ peaks [mass-to-charge ratio (*m/e*) 30, 46, 51, and 53] along with several impurity peaks due to Cl_2 (*m/e* 70, 72, and 74) and Cl_2O (*m/e* 51, 53, 86, 88, and 90). Because Cl_2 did not stick to an of the surfaces studied here, Cl_2 impuriti should not affect the present results (the presence of Cl_2O will be discussed below). Several changes in the mass spectrum of $ClONO_2$ during exposure to ice at 185 K can be seen that reveal aspects of the reaction mechanism.

The appearance of peaks at *m/e* 52 and 54 show the formation of HOCl during the reaction of $ClONO_2$ on ice. The formation of gas-phase HOCl accompanied the disappearance of the gas-phase reactants. The partial pressures *P* of $ClONO_2$ and H_2O over the cold ice surface were found to be 0.02 and 0.14 mtorr, respectively. From the extent of the decrease of $ClONO_2$ (measured with *m/e* 46), we obtained a "sticking coefficient" γ of $ClONO_2$ on ice (*12*). The sticking coefficient is the fractional collision efficiency that leads to loss of $ClONO_2$, presumably by reaction (the formation of HNO_3 from reaction 1 does not interfere with the determination of γ; see below). The sticking coefficient for $ClONO_2$ on ice

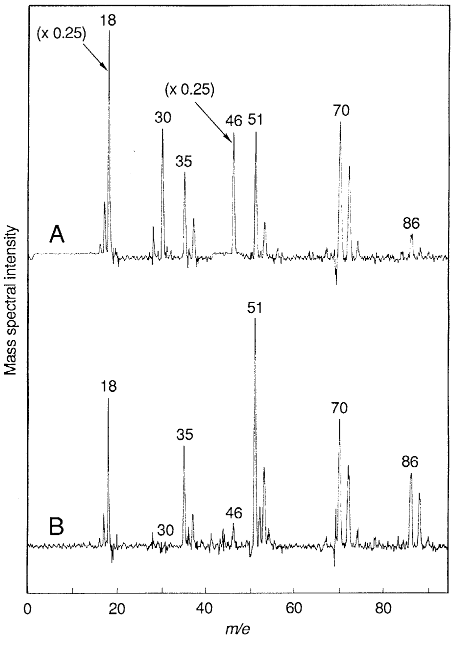

Fig. 1. Mass spectrometer scans of the Knudsen cell effluent for (**A**) $ClONO_2$ before exposure to ice ($P_{H_2O} = 0.9$ mtorr, $P_{ClONO_2} = 0.5$ mtorr) and (**B**) $ClONO_2$ exposed to an ice surface at 185 K. The two scans are shown on the same intensity scale, except that mass peaks *m/e* 18 and 46 in (A) are shown at one quarter of their actual intensity. The chlorine-atom peaks *m/e* 35 and 37 are due to fragmentation of impurity Cl_2.

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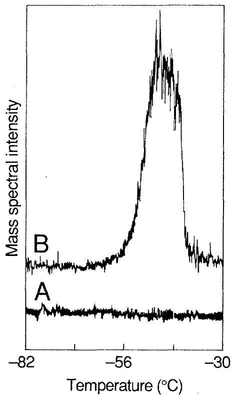

Fig. 2. Thermal desorption spectra of HNO_3 monitored by *m/e* 63 after (**A**) exposure of cold wax-coated copper to $ClONO_2$ for 1 hour and (**B**) exposure of ice to $ClONO_2$ for 1 hour, shown on the same intensity scale.

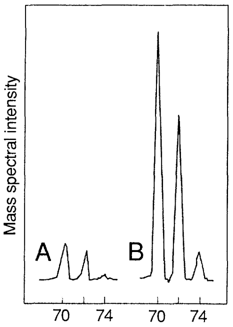

Fig. 3. Mass spectrometer scans for the Cl_2 peak intensities for (**A**) $ClONO_2$ and (**B**) $ClONO_2$ reacting with HCl on cold wax-coated copper, shown on the same intensity scale.

at 185 K was 0.009 ± 0.002 (1 SD) (*13*). This value is more than 25 times greater than the sticking coefficient for $ClONO_2$ on H_2SO_4 at room temperature (*9*), demonstrating that a faster reaction occurred with ice, although the temperature was lower.

There was a significant increase in Cl_2O mass peaks (*m/e* 86, 88, 90, 51, and 53) upon exposure of $ClONO_2$ to ice (Fig. 1), which suggests the formation of Cl_2O in a secondary reaction. Formation of Cl_2O from the dehydration of HOCl on ice (*14*) can occur by

$$HOCl + HOCl \rightarrow Cl_2O + H_2O \quad (3)$$

The equilibrium constant for this reaction strongly favors $Cl_2O + H_2O$ under our experimental conditions (*15*). Because Cl_2O has a relatively large absorption cross section at 300 nm ($\sigma = 7.05 \times 10^{-19}$ cm^2) (*16*), reaction 3 may be important in photolytic ozone depletion in the Antarctic stratosphere (since Cl_2O is formed and not lost in our experiment, the presence of impurity Cl_2O does not affect our assignment of HOCl as a product from reaction 1).

No gas-phase HNO_3 was detected in the reaction of $ClONO_2$ on ice at low temperature, as evidenced by the lack of characteristic HNO_3 peaks *m/e* 63 and 30 in Fig. 1B. Previous studies in our laboratory (*17*) and by others (*6, 7*) show that the partial pressure of HNO_3 over ice is very low at these temperatures, and thus any HNO_3 formed in reaction 1 would have remained on the surface.

The formation of HNO_3 on the surface is detected by slowly warming the ice and monitoring the desorption of HNO_3 with the parent mass peak (*m/e* 63). After exposure of copper coated with halocarbon wax to $ClONO_2$ at 185 K for 1 hour in the absence of ice, no thermal desorption of HNO_3 was observed from the surface (Fig. 2A). After similar exposure of ice to $ClONO_2$, condensed HNO_3 on the ice surface was observed in TDS (Fig. 2B).

These results indicate that $ClONO_2$ reacts with ice to form gas-phase HOCl (and Cl_2O) and condensed-phase HNO_3. If this reaction occurs on the surface of PSCs, it not only would serve as a source of active chlorine, but also would act as a sink for odd nitrogen species, a process considered important in most models of ozone depletion (*3, 4, 6, 7*).

To better simulate PSC conditions, reaction 1 was investigated at 185 K on nitric acid–ice surfaces of varying composition. The surfaces were prepared by co-condensing 1:2, 2:1, and 4.5:1 (per mole basis) gas mixtures of $H_2O:HNO_3$ at total pressures (before condensation) of 0.5, 1.0, and 1.0 mtorr, respectively. No water mass peaks were detected in the gas phase over the cold 1:2 or 2:1 surface, indicating a partial pressure of H_2O less than 0.01 mtorr. This suggests a solid phase was formed that had a very low water vapor pressure [for example, $HNO_3 \cdot 3H_2O(+)$, where (+) indicates a solid phase with an excess of HNO_3] (*6*). No HOCl was observed when $ClONO_2$ was exposed to these surfaces. However, reaction of $ClONO_2$ on the 4.5:1 $H_2O:HNO_3$ surface resulted in abundant formation of HOCl. Analysis of the gas phase over this surface revealed the presence of water ($P = 0.14$ mtorr), suggesting the formation of a solid phase with a much higher water vapor pressure. A possible assignment for this phase that is consistent with the observed water vapor pressure is $HNO_3 \cdot H_2O(-)$ (*6*). Previous studies have suggested that $HNO_3 \cdot H_2O(-)$ may be formed under Antarctic conditions (*6*). Our results indicate that reaction 1 should occur readily for this phase at low temperatures.

We have also investigated the reaction of $ClONO_2$ on cold H_2SO_4. In contrast to the room temperature results, we observe no gas-phase products for the reaction of $ClONO_2$ on 96.5% by weight H_2SO_4 at 185 K.

The reaction of $ClONO_2$ with HCl (reaction 2) may be especially important in the Antarctic stratosphere in that it converts two chlorine reservoir species into photochemically active Cl_2. We have investigated this reaction on a cold copper surface coated with halocarbon wax and on an ice surface. In both cases the reaction proceeded readily at 185 K. Before exposure to cold wax-coated copper, the reactant spectrum was identical to that shown in Fig. 1A, with the addition of the HCl peaks ($P_{ClONO_2} = 0.6$ mtorr, $P_{HCl} = 0.5$ mtorr). Exposure to the cold surface caused a dramatic increase in the Cl_2 peaks (*m/e* 70, 72, and 74), indicating that reaction 2 occurred (Fig. 3). Reaction of $ClONO_2$ with HCl on ice produced gas-phase HOCl and Cl_2. The relative amounts of the two products could not be easily determined because of the difficulty in calibration of the HOCl mass spectrometer signal.

Most of the HNO_3 formed in reaction 2 sticks on the cold surface and is detected in TDS. However, HNO_3 has a significant vapor pressure (in the absence of water), and thus some gas-phase HNO_3 is also detected. Gas-phase HNO_3 results in increased signals for *m/e* 46 and 30, and this interference makes calculation of a sticking coefficient for reaction 2 more difficult.

The importance of reaction 2 for Antarctic ozone depletion critically depends on the availability of HCl for reaction. Calculations have indicated that if only surface HCl were available for reaction, there would be insufficient HCl on the PSCs for reaction 2 to be an important source of active chlorine (*18*). We studied the reaction of $ClONO_2$ on an $HCl\text{-}H_2O$ surface at 185 K. The surface was formed by co-condensing a 7:1 $H_2O:HCl$ gas mixture at a total pressure (before condensation) of 8.0 mtorr. The water vapor pressure over this surface was ~0.09 mtorr. The reaction of $ClONO_2$ on HCl-ice proceeds until at least 95% of the total deposited HCl is depleted. This is determined by measuring the HCl content of the solid before and after reaction 2. Although the HCl was initially distributed evenly throughout the entire $HCl\text{-}H_2O$ sample, the solid phase analyzed after reaction 2 contained essentially only H_2O and HNO_3. This strongly suggests that almost all of the HCl in the bulk solid is available for reaction. This is in agreement with recent findings by Molina *et al.* that HCl undergoes rapid diffusion in ice (*19*). Molina *et al.* also report results for the reactions of $ClONO_2$ that are in essential agreement with our findings (*19*).

To the extent that PSCs are similar to the surfaces studied here, reactions 1 and 2 could be important in the photochemical mechanism responsible for ozone depletion in the Antarctic spring.

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12. The sticking coefficient is given by

$$\gamma = (A_h/A_s)[(I^0 - I)/I]$$

where A_h and A_s are the area of the Knudsen cell escape aperture and the surface area of the copper block, respectively, and I^0 and I are the $ClONO_2$ mass spectrometer signals in the absence and presence of the surface, respectively (*11*). The present value of γ was obtained with *m/e* 46 rather than *m/e* 30 to achieve higher sensitivity. The mass peak *m/e* 51 could not be used to calculate γ due to interference from Cl_2O formed in a secondary reaction.

13. This determination of γ assumes that the surface area of the ice is identical to that of the copper block. The true surface area could be larger because of the microscopic structure of the ice. To the extent that we have underestimated the ice surface area, our value of γ represents an upper limit.
14. A referee has suggested that Cl_2O can be formed by the reaction

$$HOCl + ClONO_2 \rightarrow Cl_2O + HNO_3$$

This reaction in combination with reaction 1 yields the stoichiometry given by reaction 3. We make no implications as to the detailed mechanism.

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Spacelab-2 Plasma Depletion Experiments for Ionospheric and Radio Astronomical Studies

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The Spacelab-2 Plasma Depletion Experiments were a series of studies to examine shuttle-induced perturbations in the ionosphere and their application to ground-based radio astronomy. The space shuttle Challenger fired its orbital maneuvering subsystem engines on 30 July and 5 August 1985, releasing large amounts of exhaust molecules (water, hydrogen, and carbon dioxide) that caused the electrons and ions in Earth's upper atmosphere to chemically recombine, thereby creating so-called "ionospheric holes." Two burns conducted over New England produced ionospheric peak depletions ranging from 25 to 50 percent, affected the ionosphere over a 200-kilometer altitude range, and covered 1° to 2° of latitude. Optical emissions associated with the hole spanned an area of several hundred thousand square kilometers. A third burn was conducted over a low-frequency radio observatory in Hobart, Australia, to create an "artificial window" for ground-based observations at frequencies normally below the natural ionospheric cutoff (penetration) frequency. The Hobart experiment succeeded in making high-resolution observations at 1.7 megahertz through the induced ionospheric hole.

THE SPACELAB-2 PLASMA DEPLETION Experiments conducted by the space shuttle Challenger from 29 July to 5 August 1985 represented an innovative use of the shuttle to perform space physics experiments in Earth orbit. For the first time in the shuttle program, the orbiter's small onboard engines (called the Orbital Maneuvering Subsystem or OMS engines) were fired for reasons other than to change the shuttle's orbit. These scientifically dedicated OMS firings were used to conduct a series of "active space plasma experiments" in which large quantities of neutral gases were injected into the ionosphere.

The OMS exhaust gases (H_2O, H_2, and CO_2) react rapidly with the ambient ionospheric plasma, causing the dominant atomic ions (O^+) to be converted to molecular ions (H_2O^+, OH^+, and O_2^+), which then recombine very rapidly with the ambient electrons (e^-) to form neutral species that yield optical emissions. The end result is to cause a sudden depletion in the local plasma concentrations, the creation of a so-called "ionospheric hole" (*1–3*).

The reasons for introducing such a well-defined stress into the ionosphere fall into three broad areas: (i) All shuttle missions use OMS burns for orbit insertion, for changes of orbit during a mission, and for deorbit. The prediction that ionospheric holes occur with each such maneuver needed to be verified for operational and environmental reasons. (ii) The creation of an ionospheric hole, performed in conjunction with a multidiagnostic observing program, allows one to study the "system response function" of the upper atmosphere. Earth's plasma environment involves a complex mix of processes linking solar ionizing radiation, chemical reactions between many ionized and neutral components of the atmosphere, dynamic properties (for example, winds and diffusion) of the upper atmosphere, and electrodynamic processes imposed by electric and magnetic fields of terrestrial and solar wind origin. By introducing known perturbations into a well-defined subsystem and measuring the response, we can apply standard laboratory techniques to Earth's plasma environment. Such input-output tests, coupled to computer models of the overall system, form the essence of what is meant by the phrase "active experiments" in space. (iii) Artificially induced plasma depletions, once understood and capable of being modeled in detail, can then be used to instigate other space plasma phenomena, such as the growth of plasma instabilities or the modification of radio propagation paths, thus introducing a second level of laboratory-in-space experimentation to the space sciences (*4*).

The concept behind using a Spacelab mission to investigate both the basic plasma physics and applications areas of ionospheric holes was that a shuttle mission dedicated completely to space science had the unique ability to control all aspects of the vehicle's orbit. This requirement was of crucial importance because ionospheric holes are effects left literally in the wake of the shuttle, and thus all major observations had to be made from well-equipped ground-based observatories. The OMS burns had to be conducted at certain altitudes, with precise ground tracks, and within certain local time windows and specified lunar lighting conditions.

The burns for the three experiments (Millstone 1, Millstone 2, and Hobart) are

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