28. D. S. Gilmour and J. T. Lis, *ibid.* **6**, 3984 (1986).
29. D. J. Arndt-Jovin *et al.*, *Eur. J. Biochem.* **54**, 411 (1975); H. Bunemann, P. Westhoff, R. G. Herrmann, *Nucleic Acids Res.* **10**, 7163 (1982).
30. C. Wu, C. Tsai, S. Wilson, in *Genetic Engineering*, J. K. Setlow and A. Hollaender, Eds. (Plenum, New York, in press), vol. 10.
31. M. G. Harrington *et al.*, *J. Electrophoresis* **5**, 236 (1984).
32. U. K. Laemmli, *Nature (London)* **227**, 680 (1970).
33. P. J. Mason, I. Torok, I. Kiss, F. Karch, A. Udvardy, *J. Mol. Biol.* **156**, 21 (1982); M. Goldschmidt-Clermont, *Nucleic Acids Res.* **8**, 235 (1980).
34. The K_c cells were originally obtained from the laboratory of David Hogness.
35. R. H. Reeder, J. G. Roan, M. Dunaway, *Cell* **35**, 449 (1983).
36. D. D. Brown and J. B. Gurdon, *Proc. Natl. Acad. Sci. U.S.A.* **74**, 2064 (1977).
37. T. D. Sargent, M. Janovich, I. B. Dawid, *Dev. Biol.* **114**, 238 (1986).

38. We thank C. Klee for assistance with the binding constant measurements; P. Wagner, C. Klee, I. Grummt, W. Garrard, P. de la Pena, and M. Zasloff for helpful discussions; P. Mason and B. Sauer for plasmid 122X14 and K_c cells, respectively; M. Harrington and C. Merril for the silver staining protocol; M. Brownstein for preparing synthetic oligonucleotides; B. Miller for secretarial assistance; and M. Singer for a critical review of the manuscript.

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Antarctic Stratospheric Chemistry of Chlorine Nitrate, Hydrogen Chloride, and Ice: Release of Active Chlorine

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The reaction rate between atmospheric hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$) is greatly enhanced in the presence of ice particles; HCl dissolves readily into ice, and the collisional reaction probability for $ClONO_2$ on the surface of ice with HCl in the mole fraction range from ~0.003 to 0.010 is in the range from ~0.05 to 0.1 for temperatures near 200 K. Chlorine (Cl_2) is released into the gas phase on a time scale of at most a few milliseconds, whereas nitric acid (HNO_3), the other product, remains in the condensed phase. This reaction could play an important role in explaining the observed depletion of ozone over Antarctica; it releases photolytically active chlorine from its most abundant reservoir species, and it promotes the formation of HNO_3 and thus removes nitrogen dioxide (NO_2) from the gas phase. Hence it establishes the necessary conditions for the efficient catalytic destruction of ozone by halogenated free radicals. In the absence of HCl, $ClONO_2$ also reacts irreversibly with ice with a collision efficiency of ~0.02 at 200 K; the product hypochlorous acid (HOCl) is released to the gas phase on a time scale of minutes.

THE DEPLETION OF OZONE IN THE ANTARCTIC STRATOsphere that has occurred in the spring over the past 5 or 6 years has received considerable attention (*1*). Proposed theories to explain the ozone decline include dynamical uplifting of the lower stratosphere (*2*) and chemistry involving catalytic cycles with halogen-containing free radicals as chain carriers; McElroy *et al.* suggested one that includes the reaction of chlorine monoxide (ClO) and bromine monoxide (BrO) (*3*); Solomon *et al.* (*4*) and Crutzen and Arnold (*5*) proposed another one that incorporates hypochlorous acid (HOCl) photolysis and formation by the ClO + HO_2 reaction. Another potential cycle is:

$$ClO + ClO \rightarrow Cl_2O_2 \tag{1}$$

$$Cl_2O_2 + M \rightarrow Cl_2 + O_2 + M \tag{2}$$

$$Cl_2 + h\nu \rightarrow 2Cl \tag{3}$$

$$2(Cl + O_3 \rightarrow ClO + O_2) \tag{4}$$

$$\text{Net reaction: } 2O_3 \rightarrow 3O_2 \tag{5}$$

where M is a third-body molecule and $h\nu$ is a photon.

This cycle is similar to the one we proposed earlier (*6*), except that in the second step photolysis of the ClO dimer is replaced by thermal decomposition. Room-temperature, low-pressure studies of the ClO self-reaction (*7*) have shown that the four-center channel with chlorine (Cl_2) and O_2 as products proceeds at about the same rate as the channel that yields atomic chlorine (Cl) and chlorine dioxide (ClOO), which is slightly endothermic. Because of the larger entropy barrier, the activation energy for the thermal decomposition of the dimer should be smaller for the four-center process than for the simple bond-fission processes, which generate either Cl and ClOO or two ClO radicals. Thus at 180 K the four-center channel may dominate.

These theories require significant amounts of active chlorine to be liberated from the reservoir species [hydrogen chloride (HCl) or chlorine nitrate ($ClONO_2$) or both]; furthermore, low levels of nitrogen dioxide (NO_2) are needed, or else the ClO chain carrier would be scavenged to produce $ClONO_2$. To achieve these conditions, the following heterogeneous reactions have been proposed to occur on the surfaces of polar stratospheric clouds (*4*) (PSCs), which are believed to consist mainly of ice and nitric acid (HNO_3) (*5*, *8*, *9*):

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{6}$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \tag{7}$$

We present the results of laboratory experiments that explored the interactions of gas-phase $ClONO_2$ and HCl with ice crystals. A low

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efficiency would normally be predicted for these reactions, particularly for Eq. 6, in that the almost simultaneous collision of two gas-phase molecules with an aerosol surface would be required (*3, 10*). However, we conclude that Eq. 6 can proceed efficiently in the Antarctic stratosphere in the presence of PSCs. The experiments related to the ice-HCl thermodynamic system are described more thoroughly in a separate publication (*11*), which also presents atmospheric modeling results with a detailed discussion of the implications of the HCl-$ClONO_2$-ice chemistry for ozone depletion in the Antarctic stratosphere.

Solubility of HCl in ice. Many studies have been performed to elucidate the influence of impurities on various physical properties of ice (*12*), and have indicated that only trace amounts of various compounds can be incorporated into the ordinary ice structure (I_h, hexagonal ice). HCl is specifically quoted as being only sparingly soluble in ice (*13, 14*). However, measurements of the freezing points of aqueous HCl solutions of various concentrations demonstrated the existence of several solid HCl hydrates (*15*) that have crystal structures different from that of ordinary ice (*16*).

Liquid-solid phase diagrams derived from freezing-point measurements (*15*) indicate that, for solutions that are less than ~24% by weight HCl (that is, ~7*M*, or 0.135 mole fraction), freezing yields essentially pure ice crystals, which implies a low HCl solubility. However, this lack of affinity of HCl for ice crystals is not borne out by our results. The earlier studies yielded low solubilities (*14*) because the measurements were obtained at temperatures just below 0°C. In our experiments we measured the HCl concentration directly in both phases at temperatures appropriate to achieve equilibrium. For liquid solutions with a concentration less than 24%, the HCl concentration in the solid phase is between about one-third and one-fourth of the corresponding liquid-phase value, which implies that PSCs will absorb significant amounts of HCl vapor.

Diffusion of HCl in ice. We monitored the rate of diffusion of HCl in ice crystals by measuring the HCl concentration spectrometrically at 185 nm with a mercury lamp–dielectric filter–solar blind photomultiplier assembly. Clear ice samples were prepared by slowly cooling degassed liquid water in a 4-mm diameter quartz tube. The light beam was focused to about 1 mm, and the optical transmittance of the ice sample was monitored as a function of time and distance from the surface. The partial pressure of the HCl in the gas phase was kept at a constant value (in the range from 0.01 to 1 torr) by a flowing He-HCl gas mixture at atmospheric pressure over the ice surface.

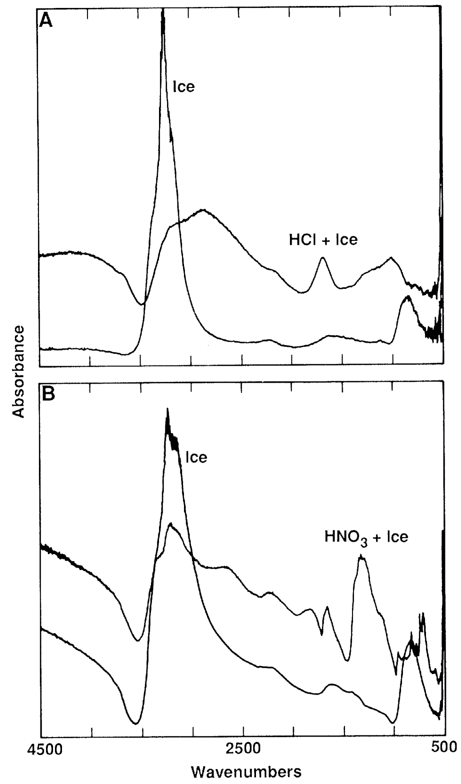


Fig. 1. Infrared spectrum at 185 K of (**A**) pure ice and ice containing about 4% by weight HCl (~0.02 mole fraction), and (**B**) pure ice and ice containing ~1% by weight HNO_3 (~0.003 mole fraction).

The HCl molecules diffuse into the ice over a distance of millimeters on a time scale of minutes. For ice samples with visible imperfections, such as cracks or gas occlusions, diffusion occurred much faster. The apparent diffusion coefficient is of the order of 10^{-5} cm^2 sec^{-1} at 185 K, a value that is best explained if we assume that the HCl molecules move along the large interstitial vacancies as opposed to displacing water molecules from the crystal lattice. However, our samples consisted of polycrystalline rather than single-crystal ice, so that diffusion along the grain boundaries may have contributed significantly to the observed rate. For PSCs with sizes in the range of 10 μm or less, diffusion of HCl should occur on a subsecond time scale.

Infrared spectra. Ice samples were prepared by condensing water vapor onto the window of a cell kept at 185 K and were placed in the optical path of a Fourier-transform infrared (FTIR) spectrophotometer (*17*). The transmission spectrum of the ice prepared in this manner (a frost) was similar to that reported previously (*18*). Subsequent deposition of HCl or HNO_3 from the gas phase substantially modified the ice spectrum (Fig. 1, A and B). The HNO_3 features near 700 cm^{-1} developed and stabilized only after 40 to 60 minutes, whereas the corresponding time for the HCl system was at most a few minutes.

Deposition of $ClONO_2$ onto ice yielded a spectrum identical to that obtained by HNO_3 deposition after ~20 minutes of stabilization. The same result was obtained on a faster time scale (less than 10 minutes) for $ClONO_2$ deposition onto ice samples pretreated with HCl vapor (Fig. 2). Deposition of $ClONO_2$ onto ice pretreated with HCl and with HNO_3 had essentially the same effect; the intensity of the HNO_3 features increased by the amount expected from stoichiometric conversion of the $ClONO_2$ (Eq. 6).

Gas chromatography on ice-coated columns. A gas chromatographic technique was used to study the interactions of various species with ice surfaces. Helium at 1 atm was used as a carrier gas, and the elemental composition of the flowing mixture was determined with microwave-induced plasma–atomic emission spectroscopy (MIP-AES) in the vacuum ultraviolet (UV) (*19*). At the parts per million levels used in this study, the signals were linear in atomic concentration (that is, for a given sample partial pressure, $ClONO_2$ produced half the chlorine-atom signal of Cl_2, half the nitrogen-atom signal of N_2, and three-halves the oxygen-atom signal of O_2). The sensitivity to nitrogen atoms was the smallest (0.2 ppm) because of the background N_2. For most experiments the gas chromatographic column was coated with ice prepared by condensation of water vapor. The signals were recorded as a function of time in the frontal analysis mode, that is, by injecting at time zero a given constant concentration of the sample (*20*). The results for Cl_2 show a species that is not retained by the ice, whereas the results for sulfur dioxide (SO_2) show that SO_2 is adsorbed (Fig. 3). The area between the Cl_2 and the SO_2 lines represents the amount of SO_2 retained by the column; a conventional adsorption isotherm can be obtained by measuring the amount adsorbed as a function of the sample concentration in the carrier gas (*21*).

For HCl and HNO_3, no measurable signal could be detected even after many hours of operation at the parts per million level. Hence, HCl is not just adsorbed on the surface at 185 K, but is incorporated rapidly into the bulk of the solid phase. In previous studies of an ice

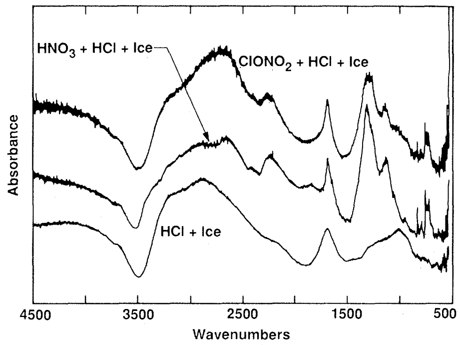


Fig. 2. Infrared spectrum of ice at 185 K, and after deposition of HCl, HNO_3, and $ClONO_2$ vapor.

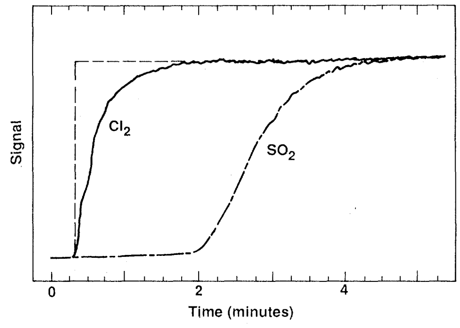


Fig. 3. Gas chromatographic signal from an ice-coated glass column at 188 K after injection of a constant concentration of sample at time zero. The dashed line is the theoretical signal expected for an inert species in the absence of mixing and diffusion effects.

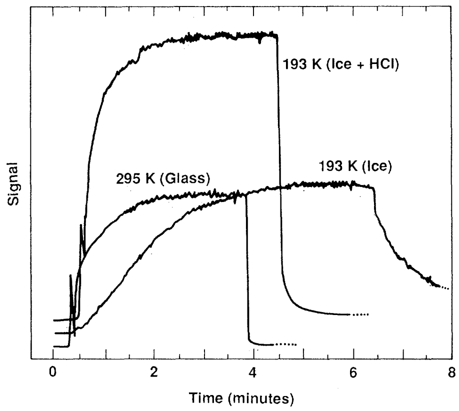


Fig. 4. Gas chromatographic chlorine-atom signal after injection of $ClONO_2$ samples for various column wall coatings.

surface, Orem and Adamson (*22*) observed similar properties for small hydrocarbons (ethane and propane); the ice appeared to retain unlimited amounts of sample, whereas for larger hydrocarbons conventional surface adsorption was observed.

The chlorine-atom signals obtained after injection of $ClONO_2$ at 185 K and coated with pure ice, or with ice doped with HCl at the 0.1 to 2% level (mole fraction 5×10^{-4} to 1×10^{-2}), are shown in Fig. 4. These results, together with those obtained by monitoring nitrogen-, oxygen-, and hydrogen-atom signals, can be summarized as follows. Injection of $ClONO_2$ on pure ice generates a delayed output signal corresponding to a species with no nitrogen atoms, one chlorine atom, one oxygen atom, and one hydrogen atom per $ClONO_2$ molecule injected. The results for ice doped with HCl correspond to a species that is eluted without measurable delay and that has two chlorine atoms per $ClONO_2$ molecule injected. The uncertainty was similar to that for signals obtained by injection of pure $ClONO_2$ samples through the uncoated glass column at room temperature, which was ~20%. These results can be interpreted if we assume that the reactions in Eqs. 5 and 7 occur in the ice, and if we assume that the product HOCl from Eq. 7 is retained to some extent by the ice; hence the delayed elution. No measurable delay was observed in the elution time for the HCl-doped column for the lowest HCl concentrations tested (about 0.1%; the signals were indistinguishable from those generated by injection of pure Cl_2).

Fast-flow reactor with ice-coated walls. To determine the efficiency per collision or the "sticking coefficient" γ for Eqs. 6 and 7, we performed an experiment in which sample pulses were introduced through a sliding injector into a cylindrical flow tube with ice-coated walls; the species were monitored with MIP-AES. The carrier gas was helium in the pressure range from 0.5 to 2.5 torr, flowing at a speed of ~1000 cm/sec. The sample pulses were roughly Gaussian, with a width at half-height in the 20- to 40-msec range and a peak partial pressure in the range from 2 to 10 mtorr (*23*).

A set of representative results are shown in Fig. 5 for HCl injection onto the ice-coated tube at 200 K; the samples disappeared within a few centimeters after injection. The hydrodynamic equations applicable to our experimental conditions, which have been solved several times (*24*), indicate that the rate-limiting step is diffusion to the walls. The rate of disappearance of the sample is insensitive to the sticking coefficient for values greater than ~0.05. For water vapor on ice, the experimental sticking coefficient near 200 K is 0.8 (*13*); within experimental error, signals from H_2O injection disappeared at the same rate as the HCl signals.

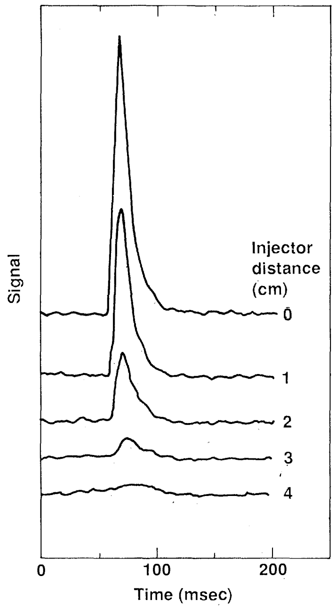
Figure 6 shows a semilogarithmic plot of the amount of sample versus the distance between the injector tip and the end of the ice coating on the reactor wall for HCl, H_2O, and $ClONO_2$ injection. The dashed lines are theoretical predictions for various γ values (*25*); the hydrodynamic equations predict straight lines, except at short distances, where injection effects may cause departures from a simple exponential behavior. The sticking coefficient for HCl on ice at 200 K is greater than 0.05, and may be near unity.

Injection of $ClONO_2$ pulses in the fast-flow tube yielded the same reaction products as the gas chromatography experiment described earlier (but with a larger experimental error for the actual stoichiometry). For the ice-coated column in the absence of HCl, we could monitor the reappearance of a signal on a time scale of minutes; it corresponded to a species containing one hydrogen-, one oxygen-, one chlorine- and no nitrogen-atoms per $ClONO_2$ molecule injected, presumably HOCl. For ice doped with HCl, the signal from $ClONO_2$ injection appeared without observable delay other than the one due to the finite flow rate. The oxygen- and nitrogen-atom signals decreased with injector distance, whereas the chlorine-atom signal increased correspondingly up to a level of two chlorine atoms per $ClONO_2$ molecule injected. Clearly, the $ClONO_2$ reacts with the HCl in the ice to release Cl_2 to the gas phase on a time scale of at most a few milliseconds. The sticking coefficient for this reaction (Eq. 6) increased between ~0.05 and 0.1 for HCl mole fractions in the ice between 0.0035 and 0.01 (Fig. 6). For Eq. 7, that is, in the absence of HCl, the sticking coefficient appears to be ~0.02. We estimate the uncertainty in the numbers to be about a factor of 2, by considering random errors, uncertainties in the calculation of the diffusion coefficient, injection effects, surface roughness, and so forth.

Heterogeneous reactions in the stratosphere. There are few laboratory studies of heterogeneous chemistry relevant to the stratosphere (*26*). The surface used in these studies was concentrated aqueous sulfuric acid (H_2SO_4), and rather low sticking coefficients ($\gamma < 10^{-3}$ to 10^{-5}) were observed even for free radical species such as chlorine atoms. Hence, the generally accepted view is that heterogeneous processes do not contribute significantly to stratospheric chemistry (*27*), with the possible exception of a few slow reactions of reservoir species such as N_2O_5, which have much longer lifetimes than the free radicals.

The $ClONO_2$ + H_2O reaction has been studied by Rossi *et al.* (*28*) on a 95% H_2SO_4 surface at room temperature. They report a relatively low sticking coefficient ($\gamma = 3 \times 10^{-4}$) which, however,

Fig. 5. Chlorine-atom emission signals from injection of HCl samples in the fast-flow reactor at 0.7 torr and 200 K as a function of time and of the length of the exposed ice coating at the reactor wall (as determined by the position of the sliding injector).



represents a large enhancement of the rate compared to that obtained with glass surfaces (*29*).

The HCl + $ClONO_2$ reaction is not expected to be important if such relatively low γ values are assumed, and particularly if we further assume simultaneous collisions of the two reactants on an aerosol surface (*10*). However, sticking coefficients approaching unity are expected for polar molecules on liquid water surfaces (*30*), with values larger than 0.1 specifically reported for a number of species such as HO_2 (*31*). Our results indicate that ice behaves more like liquid water [sticking coefficient near unity between 180 and 230 K (*13*)] than like concentrated sulfuric acid.

In our previous study of the HCl + $ClONO_2$ reaction, we placed an upper limit to the homogeneous gas phase rate of 10^{-19} cm^3 $molecule^{-1}$ sec^{-1} (*32*), and had noted that even Teflon surfaces greatly accelerated the reaction; in that study we also suggested a plausible ionic-type mechanism. Such a mechanism, which involves essentially no activation energy, probably operates in the ice matrix. The HCl molecules are incorporated readily into the solid matrix rather than interacting only with the surface. The dielectric constant of ice is comparable to that of liquid water, and species such as HCl are expected to be at least partially ionized in the ice environment. In fact, the crystal structures for the solid hydrates of HCl clearly indicate the presence of $Cl^-(H_2O)_n$ groups (*16*). Our studies show that $ClONO_2$ molecules are efficiently attached to the ice surface; this species is polar, the chlorine atom being the positive end. Its chemical properties are related to those of inorganic nitrates, hence the name "chlorine nitrate" (*33*). Also, the lower temperatures may enhance the overall reaction efficiency; there is probably no energy barrier for the approach of a polar molecule to the ice surface, and the residence time on the surface is proportional to $\exp(-\Delta H/RT)$, where ΔH is the enthalpy of adsorption (*34*), that is, the depth of the attractive well, R is the gas constant, and T is the absolute temperature. Thus, for an energy of 6 to 8 kcal/mol (typical for a hydrogen bond), the enhancement factor in residence time for a temperature change between 300 and 200 K is two to three orders of magnitude.

Our results indicate that the residence time of $ClONO_2$ on the ice near 200 K is long enough for hydrolysis to occur (Eq. 7), but Eq. 6 is faster even for HCl mole fractions of $\sim 5 \times 10^{-4}$. The high mobility of the HCl molecule in the ice matrix surely facilitates this reaction.

To fully characterize a heterogeneous reaction, in principle the rates of the various steps involved should be measured: the mass accommodation coefficient, which is the fraction of the collisions with the surface that result in the molecule entering the condensed phase, the diffusion rate in the condensed phase, the chemical reaction rate, and so forth. For surface reactions there are corresponding adsorption and desorption rates, surface diffusion rates, and so forth. These rates can be combined to yield the theoretical sticking coefficient, which is the fractional collision probability that leads to irreversible reactant loss, and for atmospheric calculations this is the most useful parameter. Our fast-flow experiments yield directly an approximate value for the sticking coefficient, and for Eq. 6 the formation of the product Cl_2 on at most a millisecond time scale places a lower limit on the rate of each of the above steps. Hence, the $ClONO_2$ molecule probably reacts at the ice surface or near it, since diffusion into the solid phase is not expected to be so rapid. For Eq. 7, we can show that the time scale of appearance of the HOCl product is in minutes rather than milliseconds. More accurate sticking coefficient values could be obtained with higher sensitivity detection techniques (for example, mass spectrometry) and larger gas-flow rates.

The thermochemistry for Eqs. 6 and 7 on ice has not yet been established; however, Eq. 6 should be exothermic ($\Delta H = -16.5$ kcal/mol for the gas-phase process), whereas Eq. 7, which is nearly thermoneutral in the gas phase (*28*), may be exothermic because of the relatively large affinity of HNO_3 for ice.

Our results indicate that the rate of reaction between $ClONO_2$ and HCl will be greatly enhanced in the presence of polar stratospheric clouds. These provide a means of concentrating the HCl and facilitating its reaction with $ClONO_2$, most likely through an ionic-type mechanism with no activation energy. This reaction has two important effects: it promotes the formation of HNO_3 with the corresponding depression of NO_2, and it generates Cl_2, which photolyzes readily to produce catalytically active free radicals that may rapidly destroy ozone in the absence of high NO_2 levels. Observations from the National Ozone Expedition (NOZE) to Antarctica during September and October 1986 have indicated unusually low concentrations of NO_2 and high concentrations of

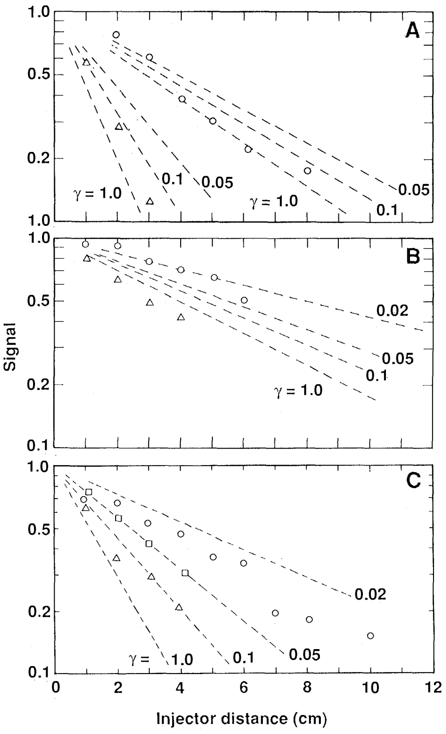


Fig. 6. Plot of the amount of sample detected as a function of injector position for the ice-coated fast-flow reactor (corresponding to pulse areas such as those shown in Fig. 5): (**A**) HCl and ice, pressures of 0.7 (△) and 2.1 (○) torr; (**B**) $ClONO_2$ on HCl-doped ice, pressure of 2.1 torr, and HCl mole fractions of 0.00 (△) and 0.01 (○); and (**C**) $ClONO_2$ on HCl-doped ice, pressure of 0.7 torr, and HCl mole fractions of 0.00 (○), 0.0035 (□), and 0.010 (△). Each point represents the average of eight pulse injections. The dashed lines are calculated for various values of the sticking coefficient γ.

$OClO$ and of ClO in the lower stratosphere, as well as variable levels of HCl and of HNO_3 (*35*). Our laboratory results provide an explanation for these field measurements, which strongly suggest a condensation process for the acids involving polar stratospheric clouds, and a heterogeneous chemical release mechanism that generates chlorine-containing free radicals and suppresses gaseous NO_2. Observations over Antarctica to be performed this year are expected to further elucidate the role of chlorine in the ozone destruction process. Additional laboratory studies of heterogeneous processes are needed, particularly to establish if $ClONO_2$ reacts with HCl in the global stratosphere as well.

REFERENCES AND NOTES

1. See, for example, the November 1986 supplementary issue of volume 13 of *Geophysical Research Letters* which contains 45 papers on the subject. See also R. J. Cicerone, *Science* **237**, 35 (1987); *ibid.* **236**, 1182 (1987).
2. J. D. Mahlman and S. B. Fels, *Geophys. Res. Lett.* **13**, 1316 (1986); K.-K. Tung, M. K. W. Ko, J. M. Rodriguez, N. D. Sze, *Nature (London)* **322**, 811 (1986).
3. M. B. McElroy, R. J. Salawitch, S. C. Wofsy, J. A. Logan, *Nature (London)* **321**, 759 (1986).
4. S. Solomon, R. R. Garcia, F. S. Rowland, D. J. Wuebbles, *ibid.*, p. 755.
5. P. J. Crutzen and F. Arnold, *ibid.* **324**, 651 (1986).
6. L. T. Molina and M. J. Molina, *J. Phys. Chem.* **91**, 433 (1987).
7. M. A. A. Clyne, D. J. McKenney, R. T. Watson, *J. Chem. Soc. Faraday Trans. 1* **71**, 322 (1975); R. A. Cox and R. G. Derwent, *ibid.* **75**, 1635 (1979); R. A. Cox, R. G. Derwent, A. E. J. Eggleton, H. J. Reid, *ibid.*, p. 1648.
8. M. B. McElroy, R. J. Salawitch, S. C. Wofsy, *Geophys. Res. Lett.* **13**, 1296 (1986).
9. O. B. Toon, P. Hamill, R. P. Turco, J. Pinto, *ibid.*, p. 1284.
10. R. R. Friedl, J. H. Goble, S. P. Sander, *ibid.*, p. 1351.
11. S. C. Wofsy, M. J. Molina, R. J. Salawitch, L. E. Fox, M. B. McElroy, unpublished results.
12. See, for example, N. H. Fletcher, *The Chemical Physics of Ice* (Cambridge Univ. Press, London, 1970), chap. 7, pp. 147–162; I. G. Young and R. E. Salomon, *J. Chem. Phys.* **48**, 1635 (1968).
13. J. G. Davy and G. A. Somorjai, *J. Chem. Phys.* **55**, 3624 (1971).
14. P. N. Krishnan and R. E. Salomon, *J. Phys. Chem.* **73**, 2680 (1969); R. G. Seidensticker, *J. Chem. Phys.* **56**, 2853 (1972).
15. S. V. Pickering, *Ber. Dtsch. Chem. Ges.* **26**, 277 (1893); F. F. Rupert, *J. Am. Chem. Soc.* **31**, 851 (1909); G. Vuillard, *C. R. Acad. Sci.* **241**, 1308 (1955).
16. Y. K. Yoon and G. B. Carpenter, *Acta Cryst.* **12**, 17 (1959); J. O. Lundgren and I. Olorsson, *ibid.* **23**, 966 (1967); I. Taesler and J. O. Lundgren, *ibid.* **34**, 2424 (1978).
17. The Nicolet 20SX FTIR spectrometer was equipped with a liquid-nitrogen cooled HgCdTe detector and was operated at 1 cm^{-1} resolution. Typically, 16 scans were averaged for each spectrum. The temperatures were monitored with copper-constantan thermocouples. The $ClONO_2$ samples were synthesized as described earlier (*32*), and the other chemicals of commercial origin (*32*) were used without further purification. The amount of water deposited on the 1-inch-diameter InSe window was typically ~5 mg, and the samples were evaporated and subsequently trapped in order to establish their composition: the HNO_3 was measured spectrophotometrically near 200 nm, and the HCl was measured by turbidimetry after treatment with a $AgNO_3$ solution.
18. N. Ockman, *Advan. Phys.* 7, 199 (1958); J. E. Bertie and E. Whalley, *J. Chem. Phys.* **40**, 1637 (1964).
19. W. Braun, N. C. Peterson, A. M. Bass, M. J. Kurylo, *J. Chromatogr.* **55**, 237 (1971); C. I. M. Beenakker, *Spectrochim. Acta* **32B**, 173 (1977).
20. The 7-mm-diameter, 3-m-long GC column was made out of glass. The Beenaker-type microwave cavity was operated at 100 watts, and the emitted light was focused onto the entrance slit of a 0.3-m McPherson 218 monochromator equipped with a Hamamatsu R1259 or R1459P solar blind photomultiplier tube. Chlorine atoms were monitored at 138 nm, nitrogen atoms at 174.5 nm, oxygen atoms at 130.6 nm, and hydrogen atoms at 121.6 nm. The carrier gas was helium at ~1 atm; it was purified by passage through a liquid-nitrogen cooled molecular sieve trap, and its flow rate, typically 360 cm^3/min, was monitored with a Matheson mass-flow meter. The samples were injected through a four-way valve after dilution with helium at a flow rate measured with a separate mass-flow meter.
21. See, for example, A. B. Littlewood, *Gas Chromatography* (Academic Press, New York, 1970), p. 137.
22. M. W. Orem and A. W. Adamson, *J. Colloid Sci.* **31**, 278 (1969).
23. The jacketed glass flow tube was 2.5 cm in diameter and 50 cm in length with cold methanol being pumped through the jacket to maintain a constant temperature. The entire gas flow was forced through a 1-cm diameter tube fitted with an Evanson microwave cavity and was operated at ~30 watts and attached to a 0.5-m Jarell Ash model 82 monochromator that was purged with helium. The gas-flow rates were measured with Matheson mass-flow meters and the pressures with MKS Baratron gauges. The sample pulses were generated by switching either a ten-way valve or a solenoid valve.
24. P. G. Gormley and M. Kennedy, *Proc. R. Irish Acad.* **52**, 163 (1949); R. E. Walker, *Phys. Fluids* **4**, 1222 (1961); R. W. Huggins and J. H. Cahn, *J. Appl. Phys.* **38**, 180 (1967); E. E. Ferguson, F. C. Fehsenfeld, A. L. Schmeltekopf, *Adv. Atom. Mol. Phys.* **5**, 1 (1969).
25. The slopes of the lines were calculated with the numerical scheme of R. L. Brown [*J. Res. Natl. Bur. Stand* **83**, 1 (1978)]. The molecular diffusion coefficients used in the calculations were estimated as in R. C. Reid, J. M. Prausnitz, T. K. Sherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 1977), p. 554.
26. A. C. Baldwin and D. M. Golden, *Science* **206**, 562 (1979); L. R. Martin, H. S. Judeikis, M. Wun, *J. Geophys. Res.* **85**, 5511 (1980).
27. R. T. Watson *et al.*, *Atmospheric Ozone 1985* (World Meteorological Organization, Geneva, 1986), chap. 2.
28. M. J. Rossi, R. Malhotra, D. M. Golden, *Geophys. Res. Lett.* **14**, 127 (1987).
29. F. S. Rowland, H. Sato, H. Khwaja, S. M. Elliott, *J. Phys. Chem.* **90**, 1985 (1986).
30. M. Mozurkewich, *Aerosol Sci. Tech.* **5**, 223 (1986); J. A. Gardner *et al.*, *J. Geophys. Res.* **92**, 10 (1987).
31. M. Mozurkewich, P. H. McMurry, A. Gupta, J. G. Calvert, *J. Geophys. Res.* **92**, 4163 (1987).
32. L. T. Molina, M. J. Molina, R. A. Stachnik, R. D. Tom, *J. Phys. Chem.* **89**, 3779 (1985).
33. M. Schmeisser and K. Braendle, *Angew. Chem.* **73**, 388 (1961).
34. A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1982).
35. R. A. Kerr, *Science* **236**, 1182 (1987); G. H. Mount, R. W. Sanders, A. L. Schmeltekopf, S. Solomon, *J. Geophys. Res.* **92**, 8320 (1987); S. Solomon, G. H. Mount, R. W. Sanders, A. L. Schmeltekopf, *ibid.*, p. 8329; R. L. de Zafra *et al.*, *Nature (London)* **328**, 408 (1987); P. M. Solomon *et al.*, *ibid.*, p. 411; C. B. Farmer, G. C. Toon, P. W. Schaper, J.-F. Blavier, L. L. Lowes, *ibid.* **329**, 126 (1987).
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