Heterogeneous Reactions of Chlorine Nitrate and Hydrogen Chloride on Type I Polar **Stratospheric Clouds**

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The heterogeneous reactions $CIONO_2 + HCl \rightarrow Cl_2 + HNO_3$ (1) and $CIONO_2 + H_2O \rightarrow HOCl + HNO_3$ (2) on vapor-deposited HNO₁-H₂O ice substrates have been investigated at 196 K by using a fast-flow reactor coupled with a quadrupole mass spectrometer. The reaction probability for (1) is 0.10 ± 0.02 and independent of both the HNO₃ and HCl concentrations in the substrate compositions studied. For (2), the reaction probability is approximately 1×10^{-5} near 53.8 wt % HNO₃, the composition of pure nitric acid trihydrate (NAT), and is about 1×10^{-3} at 46 wt % HNO₃. The sticking coefficient of HCl on these substrates was also found to be a strong function of the substrate composition, ranging from about 2×10^{-5} at NAT composition to 6×10^{-3} at 45 wt % HNO₃. The HNO₃-H₂O ice substrates were found to have large internal surface areas, and corrections for gas-phase diffusion within the porous ices were applied to observed loss rates. The large decrease in the HCl sticking coefficient and the reaction probability for (2) as the composition of pure NAT is approached from the water-enriched side can be semiguantatively explained in terms of a simple two-solid-phase model. Finally, the relation of these results to the depletion of polar ozone is discussed.

Introduction

The heterogeneous reactions of primary interest in the polar stratosphere are

$$CIONO_2 + HCl \rightarrow Cl_2 + HNO_3$$
(1)

$$CIONO_2 + H_2O \rightarrow HOCI + HNO_3$$
 (2)

$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3$$
 (3)

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{4}$$

Reactions 1-4 effectively remove NO_x from the atmosphere by producing nitric acid, which is incorporated into the condensed phase. Reactions 1-3 are important because they can convert inactive chlorine to the photolytically active forms Cl₂, ClNO₂, and HOCI. These molecules may be photodissociated to form atomic chlorine, which may remove ozone through several catalytic chain reactions.^{1,2} Reaction 1 may be particularly important since it converts the chlorine in two inactive reservoir molecules (ClONO₂, HCl) into the volatile and photochemically active Cl_2 molecule.

There is abundant recent theoretical and indirect observational evidence for two main types of polar stratospheric clouds (PSCs). The predominant form, type I, which is composed of HNO₃ and H_2O in the form of frozen nitric acid trihydrate (NAT), can condense at 195 K in the polar stratosphere. This is 5-7 K warmer than the condensation temperature of type II PSCs, which are composed mainly of H₂O ice. Since type I clouds occur more frequently than type II, they are potentially more important as surface catalysts. A detailed discussion has been given in the literature.3,4

Gas-ice interactions are a combination of the following processes: (a) diffusion to the exterior ice surface, (b) gas diffusion within the porous ice, (c) adsorption on the surface, (d) chemical reaction on the surface, (e) solid or surface diffusion, (f) desorption of products, and (g) gas diffusion of products away from the ice surface. Process c, the adsorption of gas molecules on the ice surface, can be characterized by a sticking coefficient, which is defined as the probability per gas kinetic collision that a molecule is adsorbed on the ice surface. For instance, the condensations of HCl, H₂O, or HNO₃ on ice are adsorption or sticking processes. The combination of processes c and d can be considered as a surface reaction described by a reaction probability. The reaction of chlorine nitrate with hydrogen chloride on ice to form molecular chlorine and nitric acid belongs in the category of surface reaction. 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. Both the sticking coefficient and reaction probability are symbolized by γ in this paper.

In this paper we report our investigation of reactions 1 and 2 on HNO_3-H_2O ice substrates, which have been identified as constituting type I PSCs. In the sections that follow, we describe the experimental methods used to characterize the substrates and to measure sticking coefficients and reaction probabilities. The results are summarized and discussed in terms of a simple model that accounts for the observed variation with substrate composition. Next, we compare our results with previous measurements. Finally, we discuss how the present results relate to polar ozone chemistry and calculate time constants for HCl adsorption and heterogeneous reaction on type I clouds.

Experimental Section

Description of Apparatus and Experimental Technique. The experimental apparatus consisted of a tubular fast-flow reactor coupled to a differentially pumped, modulated beam, quadrupole mass spectrometer system (Extrel Corp.) with a 70-eV electron impact ionizer.⁵⁻⁷ Figure 1 is a schematic diagram of the apparatus. Gases were continuously admitted to the reactor either through the reactor inlet or through a movable coaxial injector. Ultrahigh-purity He (Linde, 99.999%) was used as a carrier gas; typically, over 99% of the total gas flow was He. High flow rates were used to minimize back-diffusion. The ratio of the injector flow to the total flow ranged from about 1/1 to 1/10 and was usually less than 1/5. A small fraction of the gas exiting the reactor was sampled by the mass spectrometer system through a 0.1-mm pinhole located about 50 cm downstream of the reactor exit on the centerline of the reactor's gas exhaust line. The outlet reactant concentrations were monitored by tuning the mass

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Figure 1. Schematic diagram of fast-flow reactor system.

spectrometer to an appropriate mass peak. Frozen HNO₃-H₂O substrates were formed by vapor deposition onto the reactor walls. When the injector position was varied, the contact time of the reactants on the substrate could be changed and the reaction rate determined as described below. Two liquid nitrogen trapped 320 L s⁻¹ diffusion pumps evacuated the mass spectrometer detection system to about 10⁻⁷ Torr during the experiments. The mass spectrometer ion signal was detected with an electron multiplier operated in a pulse counting mode. The beam sampled through the pinhole was modulated by a 100-Hz chopper allowing the mass spectrometric background to be monitored during the experiments. Gated counters accumulated the total signal and the background signal for 5-20 s.

Two separate 40-cm glass reactors one having an inner diameter of 1.76 cm and the other an inner diameter of 2.80 cm were used in the experiments. The reactors were double-jacketed; methanol, normally cooled to 196 K, circulated through the inner jacket, and the space between the inner and outer jackets was evacuated to thermally insulate the reactor. The methanol temperature at the midpoint of the reactor's length was maintained at 196 ± 1 K. The temperature varied by less than 1.0 K over the length of the reactor.

The movable injector consisted of a jacketed glass tube with an inner diameter of 0.4 cm and an outside diameter of 1.25 cm. To prevent condensation within, the injector was warmed by passing gaseous nitrogen through its jacket. A Viton O-ring dynamically sealed the injector inlet to the reactor. To prevent atmospheric water from entering the reactor when the injector was moved, it was necessary to use a nitrogen purged double-Oring seal at the injector inlet on the small diameter flow tube. The gas flow lines exterior to the reactor were constructed of either stainless steel or Teflon tubing; other gas handling and storage components were constructed of glass with clamped Viton O-ring joints. Gas flow rates were controlled with stainless steel needle valves and measured with monel mass flow meters that were individually calibrated with He.

The gases were pumped through the reactor by a liquid nitrogen trapped 25 L s⁻¹ oil-sealed rotary vacuum pump. The total pressure in the reactor varied between 0.3 and 2.0 Torr during the experiments, and the flow velocities varied between 80 and 2500 cm s⁻¹. A 20-mm Teflon valve located in the glass line between the reactor exit and the mass spectrometer could be used

to isolate the reactor from the mass spectrometer. The total pressure in the reactor was monitored with a capacitance manometer (MKS Baratron) accurate to ±0.5 mTorr.

Chlorine nitrate was prepared by the method of mixing Cl₂O and N₂O₅ at 196 K in the dark and was further distilled from 196 to 77 K. The purity was checked by ultraviolet spectrophotometry and mass spectrometry, and it was found to be greater than 90%. Trace impurities such as Cl₂ and Cl₂O do not interfere with our measurements of γ . To measure the reaction probability of CIONO₂ on HNO₃-H₂O ices, CIONO₂ was carried into the injector by He flowing through a ClONO₂ bubbler maintained at 195 K in a dry ice-alcohol bath. The concentration of ClONO₂ in the gas stream exiting the bubbler was calculated by assuming that the gas mixture was ideal and that the He was saturated with ClONO₂ at its vapor pressure of about 1.2 Torr, which was measured in our laboratory. The change in the ClONO₂ reactor exit concentration with injector position was monitored by the NO_2^+ ion fragment at m/e = 46. The production of HOCl was detected at the parent ion peak, m/e = 52.

To obtain a signal proportional to $ClONO_2$, the signal at m/e= 46, due to HNO₃ evaporating from the substrate, was measured with no ClONO₂ present and subtracted from the total. The magnitude of the interfering HNO₃ signal (5-25% of ClONO₂) depended on the substrate composition and was a function of injector position. The HNO₃ signal decreased by a factor of 2-3 to a constant value when the injector was withdrawn 5 cm relative to the reactor exit. This is probably due to the injector warming the substrate (see Substrate Preparation).

The sticking coefficient of HCl on HNO₃-H₂O substrates was measured in a manner similar to the ClONO₂ reaction probability. The HCl⁺ parent ion signal at m/e = 36 was used to monitor the change in the HCl reactor exit concentration. High-purity HCl (Matheson, 99.99%) was used without further purification.

The HNO₃-H₂O ices were doped with HCl prior to measuring the reaction probability of CIONO₂ with HCl. During some of these experiments, HCl was passed continuously into the reactor through the upstream inlet while CIONO₂ was added through the sliding injector. During other experiments, the HCl valve was closed, and in this case, its partial pressure in the reactor was the result of evaporation from the substrate. The exit concentration of CIONO₂ was monitored by the NO₂⁺ ion fragment at m/e =46, and the reaction product, Cl_2 , was monitored by the parent ion peak at m/e = 70.

Interaction of Flow Dynamics, Surface Reaction, and Diffusion. Typical experimental conditions with flow velocities between 500 and 2000 cm s⁻¹ and total pressures between 0.3 and 1.0 Torr yield Reynolds numbers less than 10. Under these conditions, the flows are essentially laminar. The entrance length or the distance required for the flow to develop a parabolic velocity profile is less than 1 cm, and estimated mass diffusion mixing times for CIONO₂ in He are 0.5-1 ms.⁸ Data points taken at reaction lengths less than 1 cm could be subject to the effects of incomplete mixing and less than full laminar flow. These data points were not included in the rate determinations.

Besides the effects just described, it is also necessary to consider the possible effect on observed rate constants of the interaction of flow dynamics with surface reaction and diffusion. Only a brief discussion of these interactions is presented here; more details are given elsewhere.9 Under the experimental conditions used in flow tube reactors, observed decay rates can be affected by the finite rate of diffusive mass transfer to the exterior of the ice substrate (external diffusion, process a above). Interaction of flow dynamics and external diffusion has been discussed previously,^{8,10-13} and the correction procedure has been validated experimentally.⁸

Decay rates observed in the present study have been corrected for external axial and radial diffusion by using the method de-

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Figure 2. Temperature profile in the reactor with an i.d. of 1.76 cm. A similar temperature profile was also found for the larger reactor with 2.80-cm i.d.

scribed by Brown.¹² For these corrections, a value of 170 Torr cm² s⁻¹ was used for the pressure-independent diffusion coefficient (pD_{e}) of ClONO₂ in He and 270 Torr cm² s⁻¹ for HCl in He; these were estimated from experimental values for Kr in He and Ar in He¹⁴ after the differences in reduced mass and molecular diameters were adjusted. Under typical conditions, external diffusion corrections were less than 20% for $\gamma < 0.01$; for $\gamma >$ 0.1, corrections were a factor of 2 or larger.

In addition to external diffusion, observed surface loss rates can be affected by gas-phase diffusion of the reactive species within the porous interior of the solid (internal diffusion, process b above). The theory of surface reaction limited by internal gaseous diffusion within porous catalysts is well-known,¹⁵⁻¹⁷ but it apparently has not been applied specifically to flow reactor studies of the present type. For porous solids, the reactive surface consists of both the external surface and any internal surfaces connected to the exterior of the solid. In the case of a tubular reactor with a thin substrate of thickness h deposited on its interior surface, it can be shown⁹ that

$$k_{\rm s} = k_{\rm sg} / (1 + \eta h \rho_{\rm b} S_{\rm g}) \tag{5}$$

where k_s is the true surface rate constant, k_{sg} is the observed decay rate corrected for external diffusion, η is the effectiveness factor of the internal surface, ρ_b is the bulk density of the substrate, and $S_{\rm g}$ is its specific surface area. The quantity $(1 + \eta h \rho_{\rm b} S_{\rm g})^{-1}$ gives the correction for internal diffusion. The relationship between η and k_s has been discussed elsewhere.⁹

The effectiveness factor (η) is the fraction of internal surface taking part in the reaction and depends on the relative rates of surface reaction and gas-phase diffusion within the porous solid. For inactive surfaces, the rate of surface reaction is slow compared to diffusion within the porous solid, and most of the internal surface participates in the reaction; that is, $\eta \approx 1$. Conversely, when



Figure 3. Typical data plot for the $CIONO_2 + H_2O \rightarrow HOCl + HNO_3$ reaction, showing loss of CIONO₂ signal and growth of product HOCl.



Figure 4. Demonstration of surface poisoning for the $CIONO_2 + H_2O$ HOCI + HNO₃ reaction on a 45.6 wt % HNO₃ substrate. Reaction probability corrected for external diffusion is plotted vs total contact time. For times less than about 5 min, the effect is negligible. See text for detail.

surface reaction is fast compared to diffusion, reaction occurs mainly in the outer region of the porous solid and η approaches zero.

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TABLE I: Summary of Experimental Measurements of the Reaction Probability of CIONO2 with H2O on HNO3-H2O Substrates^a

substrate				pressur	c						
wt % HNO3	mass, g	length, cm	thickness, ^c µm	P(ClONO ₂), mTorr	total, Torr	velocity, cm s ⁻¹	k _s (obs), s ⁻¹	k_{sg}, s^{-1}	γ_{g}	k_{s}, s^{-1}	γ_{s}
37.6	0.62	15.0	91.2	0.074	0.387	1930	211	236.5	0.020	12.5	1.1 × 10 ⁻³
44.6	0.57	4.7	116	0.050	0.358	1750	227	257	0.021	13.4	1.1 × 10 ⁻³
45.5	0.67	25.0	59.1	0.049	0.363	1750	215	242	0.020	15.9	1.3×10^{-3}
45.6	0.55	12.5	72.8	0.046	0.354	1760	260	300	0.025	19.6	1.7 × 10 ⁻³
45.7	0.80	30.5	57.8	0.085	0.384	1920	145	157	0.013	9.26	7.8 × 10 ⁻⁴
45.7	0.88	30.7	63.2	0.082	0.385	1920	182	201	0.017	11.9	1.0×10^{-3}
46.4	0.75	15.2	108	0.075	0.385	1920	257	296	0.025	17.3	1.5×10^{-3}
49.9 ^b	0.92	30.5	66.3	0.076	0.383	1920	125	134	0.011	6.9	5.8 × 10 ⁻⁴
51.0	1.08	29.5	80.7	0.075	0.383	1310	36.7	37.4	3.1×10^{-3}	1.39	1.2×10^{-4}
51.0*	1.00	30.7	71.9	0.075	0.383	1910	22.2	22.5	1.9×10^{-3}	0.91	7.6 × 10 ⁻⁵
51.80	1.09	32.5	73.8	0.073	0.387	1890	14.3	14.4	1.2×10^{-3}	0.56	4.7×10^{-5}
51.8	0.94	31.0	66.6	0.076	0.388	1900	11.3	11.4	9.6 × 10 ⁻⁴	0.48	4.1 × 10 ⁻⁵
51.80	0.96	29.5	71.8	0.075	0.386	1880	9.00	9.04	7.6 × 10 ⁻⁴	0.36	3.0×10^{-5}
52.1 ^d	1.30	33.2	86.4	0.95	0.94	590	7.58	7.67	6.5 × 10 ⁻⁴	0.25	2.1×10^{-5}
520	0.94	29.1	71.3	0.032	0.572	2440	22.3	22.6	1.9 × 10 ⁻³	0.92	7.7×10^{-5}
53.8	1.04	31.2	58.4	1.32	0.435	452°	2.25	2.27	3.1×10^{-4}	0.11	1.5×10^{-5}
55.2	0.57	24.7	25.3	1.31	0.421	546°	0.71	0.71	9.7 × 10 ⁻⁵	0.073	9.9 × 10 ⁻⁶

^a Unless noted otherwise, the flow tube radius is 0.88 cm and the temperature is 196 ± 1 K. ^b Estimated from the HNO₃-H₂O bubbler composition. ^cCalculated assuming a substrate density of 0.84 g/cm³. ^d Water frost from air leakage was observed upstream of the substrate; this may affect the accuracy of the measurement. ^cFlow tube radius equals 1.4 cm.



Figure 5. ClONO₂ + H₂O \rightarrow HOCl + HNO₃, summary plot of reaction probability (after correction for external and internal diffusion) vs weight percent HNO₃ in the substrate. The curves through the data were calculated from a model that assumes that the substrate comprises a twophase mixture of NAT and H₂O ice each with its characteristic reaction probability. For NAT, $\gamma_{NAT} = 1 \times 10^{-5}$ (all three curves), and for H₂O ice, $\gamma_1 = 1 \times 10^{-2}$ (top curve), 5×10^{-3} (middle curve), and 1×10^{-3} (bottom curve). The best least-squares fit is at $\gamma_1 = 5 \times 10^{-3}$. See text for detail.

In order to use eq 5 to correct for internal diffusion, several parameters characteristic of the ice substrate must be known: the bulk density, the specific surface area, and the sample thickness were obtained experimentally (see below), and the effectiveness factor was evaluated by using an experimentally verified model. Details of this procedure are presented elsewhere.⁹ Internal diffusion corrections range from about a factor of 1/3 for reactive ice surfaces to a factor of 1/25 for inactive surfaces.



Figure 6. Summary plot of HCl sticking coefficients (after correction for external and internal diffusion) vs weight percent HNO₃ in the substrate. The curves through the data were calculated from a model that assumes the substrate comprises a two-phase mixture of NAT and H₂O ice, each with its characteristic sticking coefficient. For NAT, $\gamma_{NAT} =$ 1×10^{-5} (all curves), and for H₂O ice, $\gamma_1 = 0.06$ (top curve), 0.04 (middle curve), and 0.02 (bottom curve). The best least-squares fit is at $\gamma_1 =$ 0.04. See text for detail.

$$\gamma_s$$
 is related to k_s by

$$\gamma_{\rm s} = 2ak_{\rm s}/(\omega + ak_{\rm s}) \tag{6}$$

where γ_s is the true reaction probability or sticking coefficient, *a* is the reactor's inner radius, and ω is the average molecular velocity. A similar relationship relates γ_g , the reaction probability or sticking coefficient corrected only for external diffusion, to k_{sg} .

Substrate Preparation. Vapor deposition, instead of freezing the liquid, was used to prepare the substrates to prevent nonusubstrate

TABLE II: Summary of Experimental Measurements of the HCl Sticking Coefficient on HNO₃-H₂O Substrates^a

pressure

	Substitute			P1033	uiv							
wt %	mass,	length,	thickness, ^c	P(HCl),	total,	radius,	velocity,	$k_{\rm s}({\rm obs}),$				
 HNO ₃ °	g	cm	μm	mTorr	Torr	cm	cm s ⁻¹	s ⁻¹	k_{sg}, s^{-1}	γ_{g}	$k_{\rm s}, {\rm s}^{-1}$	γ_{s}
 44.2	0.56	19.9	62.1	0.16	0.361	0.88	1790	656	910	0.046	91	4.7×10^{-3}
45.2	0.78	30.7	56.0	0.22	0.361	0.88	1770	805	1220	0.061	152	7.8 × 10⁻³
45.7	0.77	29.7	57.2	0.26	0.363	0.88	1800	695	983	0.049	105	5.4 × 10 ⁻³
45.7	0.62	20.1	67.9	0.23	0.361	0.88	1780	814	1240	0.061	155	7.9 × 10 ⁻³
49.9 ^d	0.85	30.5	61.5	0.26	0.361	0.88	1800	309	358	0.018	22.2	1.1×10^{-3}
51.0 ^d .g	0.89	29.5	66.5	0.24	0.361	0.88	1810	228	254	0.013	13.6	7.0 × 10 ⁻⁴
51.0 ^{d.g}	0.92	30.0	67.4	0.25	0.360	0.88	1820	114	120	6.1 × 10⁻³	5.56	2.9 × 10 ⁻⁴
51.8 ^d .8	0.93	29.5	69.6	0.26	0.354	0.88	1750	59.3	61.0	3.1 × 10⁻³	2.59	1.3 × 10 ⁻⁴
51.98	0.66	29.9	30.6	2.02	0.446	1.40	365	48.9	62.3	5.1 × 10 ⁻³	5.61	4.7 × 10 ⁻⁴
52.0 ^{d.g}	1.65	29.7	77.1	1.42	0.456	1.40	443	50.9	61.3	5.0 × 10 ⁻³	2.48	2.1 × 10 ^{−4}
52.0 ^d	1.55	30.4	70.7	1.37	0.451	1.40	433	104	153	0.012	7.8	6.4 × 10 ⁻⁴
52.0 ^d	1.54	30.2	70.7	1.50	0.453	1.40	440	115	174	0.014	9.2	7.6 × 10 ⁻⁴
52.0 ^d	0.66	28.8	31.8	1.73	0.448	1.40	407	86.3	123	0.010	11.1	9.2 × 10 ^{−4}
52.0 ^d	0.71	29.7	33.2	1.58	0.452	1.40	431	52.5	64.1	5.3 × 10 ⁻³	5.38	4.5 × 10 ^{−4}
52.0 ^d	1.43	31.7	62.6	1.75	0.444	1.40	391	38.3	45.5	3.7×10^{-3}	2.51	2.1 × 10 ⁻⁴
52.0 ^{d.g}	1.41	29.8	65.6	1.62	0.423	1.40	381	78.4	113	9.2 × 10 ⁻³	5.68	4.7 × 10 ^{−4}
52.3 ^{d,f}	1.09	32.5	73.8	0.24	0.364	0.88	1780	9.6	9.6	4.9 × 10 ⁻⁴	0.37	1.9 × 10 ⁻⁵
52.3 ^{d,f}	0.94	31.0	66.6	0.30	0.388	0.88	1900	8.7	8.7	4.5 × 10 ⁻⁴	0.37	1.9 × 10 ⁻⁵
52.3 ^d ,	0.94	31.0	66.6	0.30	0.388	0.88	1900	13.1	13.2	6.8 × 10 ⁻⁴	0.56	2.9 × 10 ⁻⁵
52.48	0.63	30.1	29.0	1.72	0.439	1.40	378	68.4	94.0	7.7 × 10⁻³	9.03	7.5 × 10⁴
52.5ª	0.91	30.5	65.9	0.19	0.553	0.88	2390	11.5	11.6	5.9 × 10 ⁻⁴	0.49	2.6 × 10⁻⁵
52.5ď	1.08	31.5	75.4	0.19	0.556	0.88	2380	18.8	19.0	9.7 × 10 ⁻⁴	0.72	3.7 × 10 ⁻⁵
52.9 ^{d,e}	1.19	28.2	93.1	20.1	1.00	0.88	599	10.1	10.2	5.2 × 10 ⁻⁴	0.31	1.6 × 10 ⁻⁵
53.88	1.26	30.2	57. 9	1.65	1.76	1.40	91.0	7.6	8.9	7.3 × 10 ^{−4}	0.43	3.6 × 10 ⁻⁵
54.0 ^g	1.73	30.1	79.7	1.78	0.51	1.40	88	5.3	7.3	6.0 × 10 ⁻⁴	0.26	2.2×10^{-5}
54.0 ^s	1.44	31.2	64.0	1.77	1.67	1.40	94.0	7.01	8.08	6.7 × 10 ⁻⁴	0.36	2.9 × 10 ⁻⁵
54.6	0.56	15.0	51.8	1.63	1.77	1.40	159	14.8	16.9	1.4 × 10⁻³	0.91	7.6 × 10 ⁻⁵
55.2 ⁸	1.08	26.7	56.1	1.57	1.92	1.40	91.2	1.40	1.44	1.2 × 10 ⁻⁴	0.071	5.9 × 10⊸
55.2	1.69	31.2	75.1	1.58	1.78	1.40	449	14.6	15.4	1.3×10^{-3}	0.59	4.9 × 10 ⁻⁵
55.6	2.15	30.3	98.4	1.71	1.73	1.40	431	7.26	7.46	6.2 × 10 ⁻⁴	0.22	1.8 × 10 ⁻⁵
55.7	1.37	30.7	61.9	2.07	1.91	1.40	82.6	0.425	0.429	3.5 × 10 ⁻⁵	0.019	1.6 × 10⁻⁵
55.8	0.67	29.9	31.1	1.77	1.78	1.40	100	0.410	0.413	3.4×10^{-5}	0.035	2.9 × 10 ⁻⁶
57.0	0.93	30.4	42.4	1.74	1.70	1.40	90.8	<0.17	<0.17	<1.4 × 10 ⁻⁵	<0.011	<9.0 × 10 ⁻⁷
57.4	1.31	30.7	59.2	1.98	1.87	1.40	79.8	<0.22	<0.22	<1.8 × 10 ⁻⁵	<0.010	$< 8.5 \times 10^{-7}$

^a The temperature is 196 ± 1 K. ^b Calculated with the HCl mass excluded. ^c Calculated assuming a substrate density of 0.84 g/cm³. ^d Estimated from the HNO₃-H₂O bubbler composition. ^e Water frost from air leakage was observed upstream of the substrate; this may affect the accuracy of the measurement. ^f Corrected for estimated substrate composition change (~0.5 wt %) from ClONO₂ reaction probability measurement before HCl sticking coefficient measurement. ^g Data were taken after an "induction period" of a few minutes.

niformities due to phase separations during the freezing process. To prepare the frozen HNO₃-H₂O substrates, He at approximately atmospheric pressure was bubbled through a nitric acid solution maintained at 293 K; the resulting gaseous mixture entered the reactor through the injector. The injector was withdrawn in either 2- or 5-cm steps to coat the reactor walls. A white frostlike solid was observed to deposit on the cold reactor walls. The total pressure in the reactor during the coating procedure was about 1 Torr. If we assume the bubbler outlet gas mixture was saturated with nitric acid and water at 293 K, the reactor partial pressures of nitric acid and water were within the nitric acid trihydrate stability envelope.¹⁸ Typically, the deposition rate was approximately 0.5 g h⁻¹; this formed a 70- μ m-thick substrate over about 30 cm of the reactor's length in 2 h. The length of the coated section or the coating time was changed in order to vary the coating thickness.

When the concentration of nitric acid in the bubbler solution was varied, the concentration of nitric acid in the frozen substrates could be varied from 44 to 60 wt % nitric acid (pure nitric acid trihydrate is 53.8 wt % nitric acid). After the coating was completed, the nitric acid bubbler valve was closed and no more nitric acid or water could enter the reactor. We observed that the flow of He over water-rich substrates preferentially removes water; substrates that remained in the reactor for 4–6 h were found to have increased their bulk composition by as much as 2 wt % (see Substrate Analysis), sometimes approaching the composition of pure NAT.

Heat transfer from the warm injector significantly warmed the inside surface of the reactor wall. The temperature of the reactor wall surface was measured, either in the presence or in the absence of any substrate, by inserting a thermocouple into the flow tube so the thermocouple was in contact with the inside wall. Figure 2 shows the inner surface temperature of the 1.76-cm reactor relative to the injector outlet location. Although the surface temperature directly opposite the injector was 10-30 K warmer than the methanol coolant, the temperature 1 cm downstream of the injector outlet was effectively the same as the methanol coolant. Since 1 cm approximates the mixing distance for reactants exiting the injector, the operative temperatures of the substrates during reaction probability measurements and substrate depositions were taken equal to the coolant temperature. However, the warm injector effectively annealed the nitric acid-water substrates at 205-220 K.

Substrate Analysis. Following each run, the substrate was collected by vacuum distillation for weighing and for chemical analysis. Total acid was determined by titration with standardized NaOH solutions to the phenophthalein end point. Chloride ion was determined by using a calibrated ion-selective electrode (Orion No. 9417B), which operates at pH >2. During the chloride analysis, substrate solution acidity was checked with a pH meter and increased to approximately 2 by dropwise addition of 10 and 1 M NaOH. Separate aliquots of substrate solution were used for the pH adjustment and for the actual chloride ion analysis to prevent introduction of chloride ion from the pH electrode. Samples of the reservoir (bubbler) solution were used to check the reagents for background chloride, which generally was near the detection limit of 2×10^{-5} M.

Surface Areas. To obtain reaction probabilities from observed loss rates, substrate surface areas are needed. These measurements are described elsewhere,¹⁹ and only a brief summary is given here.



Figure 7. $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$, summary plot of reaction probability (corrected for external diffusion only) vs weight percent HNO₃ in the substrate.

Substrates were formed in a separate apparatus by vapor deposition at 195 K under conditions similar to those used to prepare surfaces for the flow tube measurements. Deposition rates were in the range of 0.08-1.4 g h⁻¹, with total sample weights between 0.15 and 1.0 g. Compositions were varied between pure H₂O ice and 82 wt % HNO₃. Some substrates were warmed to 205-220 K, which approximates the highest temperatures to which the flow tube surfaces were then determined by using the Brunauer, Emmett, and Teller (BET) method to analyze 77 K adsorption isotherms of N₂, Ar, or Kr.

For samples with compositions near NAT, and held at 195 K, the average surface area was $3.4 \pm 1.5 \text{ m}^2 \text{ g}^{-1} (1\sigma \text{ precision only})$. For 1-g samples, this value is about 200 times larger than the geometric surface area calculated for a substrate, 70 μ m thick by 30 cm in length, deposited on the inner surface of the 1.76cm-diameter flow tube reactor. The BET surface areas are very sensitive to warming above the 195 K deposition temperature. To check the effect of annealing on the surface areas, six samples were warmed to 205-220 K for 20-60 min. Surface areas of these annealed samples averaged $0.42 \pm 0.11 \text{ m}^2 \text{ g}^{-1} (1\sigma \text{ precision only})$, about a factor of 8 lower than the unannealed samples but still about 25 times larger than the geometric area. We used the surface area of $0.42 \text{ m}^2/\text{g}$ for our data analysis.

Substrate Bulk Densities. For porous solids the process of gas-phase diffusion through the void space of the solid must be considered. To obtain the needed diffusion rates, bulk densities (ρ_b) were obtained directly from sample weights and apparent solid volumes. Photographs were used to obtain the ice volumes by measuring the differences between the height profiles of the substrates at different times during the deposition. Details of this procedure are given elsewhere.¹⁹ For NAT between 195 and 230 K, the observed bulk density of six samples averaged 0.84 ± 0.06 g cm⁻³ (1 σ precision only). This is much lower than the true solid density of 1.62 g cm⁻³ obtained from X-ray structure studies of single crystals²⁰ and implies an open-pore structure in the va-



Figure 8. $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$, summary plot of reaction probability (corrected for external diffusion only) vs weight percent HCl in the substrate.

por-deposited HNO_3 - H_2O ices through which diffusion can occur. Infrared Spectra. In separate experiments, the chemical composition of HNO₃-H₂O substrates was also investigated by means of Fourier transform infrared spectroscopy. We constructed a conventional "matrix isolation" type infrared cell in which a cold AgCl window was used to support ice films formed by vapor deposition. A series of experiments were performed at 188 K (window temperature) with various compositions from pure water ice to pure nitric acid. At 54 wt % HNO3, the data suggest that the substrate contains pure NAT. The identification was based on the characteristic infrared absorption spectra of oxonium ions and nitrate ions. The substrate with less than 54 wt % was found to consist of substantial quantities of water ice, which was identified by its adsorption near 3220 cm⁻¹, superposed on the NAT spectrum. Detailed information about the infrared study is given in a separate article.²¹ The infrared spectra are consistent with the phase diagram of the nitric acid-water ice system as expected. This information is very useful in interpreting our kinetic data (see below).

Results

For an irreversible first-order reaction the following equation holds for the reactant

$$n [S_t(z)] = -k_s(obs)(z/v) + \ln [S_t(0)]$$
(7)

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

$$\ln [S_t(z) - S_t(\infty)] = -k_s(obs)(z/v) + \ln [S_t(0) - S_t(\infty)]$$
(8)

where $S_t(\infty)$ is the signal when the reaction has reached completion. The left-hand sides of eqs 7 and 8 were plotted vs the injector position for reactant loss and product formation, respectively. Observed reaction rate constants ($k_s(obs)$) were obtained from linear least-squares fits to these data.

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substrate

TABLE III: Summary of Experimental Measurements of the Reaction Probability of HCl with ClONO2 on HNO3-H2O Substrates⁴

nressure

	wt % HNO ₃ ¢	wt % HCl	mass,	length, cm	thickness, ^c µm	P(HCl), mTorr	P(CIONO ₂), mTorr	total, Torr	velocity, cm s ⁻¹	m/e	$k_{s}(obs), s^{-1}$	k, s ⁻¹	γ.
_	41.8	2 50	0.81	20.3	88.0	VD	0.077	0 384	1010	46	1250	3500	0.26
	41.8	2.50	0.81	20.3	88.0	VPd	0.077	0.384	1910	70	1120	2630	0.20
	44.2	1 46	0.51	19.9	62.1	VP ⁴	0.077	0.304	1920	46	853	1490	0.12
	45.7	212	0.50	20.1	68.0	VP4	0.009	0.375	1910	46	1110	2580	0.12
	46.1	3.91	0.78	30.7	56.0	VP4	0.089	0 383	1910	46	1620	1.06 × 10 ⁴	0.62
	46.1	3.91	0.78	30.7	56.0	VP ^d	0.089	0.383	1910	70	1250	3490	0.26
	46.4°	0.574	0.50	14.5	76.6	VP ⁴	0.087	0.387	1900	70	653	982	0.081
	47.1	0.934	0.47	19.5	53.1	VP ⁴	0.073	0.388	1920	46	1250	3550	0.26
	47.1	0.934	0.47	19.5	53.1	VP ^d	0.073	0.388	1920	70	1000	2060	0.16
	53.0	0.30	0.96	29.5	71.7	0.25	0.075	0.386	1900	46	1820	7.13 × 10 ⁴	1.00
	53.1	0.595	0.89	29.5	66.4	0.20	0.075	0.383	1930	46	1480	6320	0.42
	53.1	0.595	0.89	29.5	66.4	0.20	0.075	0.383	1930	70	1090	2450	0.19
	53.1	0.595	0.89	29.5	66.4	VP ^d	0.075	0.383	1930	70	802	1350	0.11
	53.3	0.506	1.16	30.0	86.0	1.24	0.14	0.651	2110	70	781	1990	0.15
	53.4	0.0428	1.08	31.5	75.4	0.14	0.059	0.578	2430	70	558	889	0.072
	53.4	0.0711	1.02	32.0	70.1	0.12	0.058	0.588	2470	70	1020	3730	0.27
	53.4	0.463	0.92	30.0	67.4	0.22	0.078	0.384	1860	46	1400	5190	0.36
	53.4	0.463	0.92	30.0	67.4	0.22	0.078	0.384	1860	70	1180	3030	0.23
	53.4	0.463	0.92	30.0	67.4	VP ^d	0.078	0.384	1860	70	1780	3.54×10^{4}	1.00
	53.5	0.213	1.06	30.0	78.0	1.51	0.28	0.649	2180	70	1070	7680	0.49
	53.5	0.213	1.06	30.0	78.0	5.56	0.28	0.649	2180	70	944	3710	0.27
	53.5	0.213	1.06	30.0	78.0	1.51	0.28	0.649	2180	70	646	1270	0.10
	53.5	0.107	0.93	29.5	69.6	0.24	0.078	0.376	1870	46	1500	6600	0.43
	53.5	0.107	0.93	29.5	69.6	V₽₫	0.078	0.376	1870	46	1410	5100	0.35
	53.6	0.0375	0.91	30.5	65.9	0.17	0.058	0.574	2450	70	813	1820	0.14
	53.6	0.0375	0.91	30.5	65.9	VP ^d	0.058	0.574	2450	70	549	863	0.070
	53.6	0.0375	0.91	30.5	65.9	0.16	0.058	0.574	2450	70	653	1160	0.093
	53.6	0.185	1.09	32.5	73.8	0.20	0.073	0.386	1890	70	1270	3730	0.27
	53.6	0.185	1.09	32.5	73.8	0.20	0.073	0.386	1890	46	1580	9450	0.57
	53.6	0.185	1.09	32.5	73.8	VP ^d	0.073	0.386	1890	46	1220	3320	0.25
	53.6	0.206	0.94	31.0	66.5	0.273	0.076	0.388	1890	46	1310	4140	0.30
	53.6	0.206	0.94	31.0	66.5	0.273	0.076	0.388	1890	70	1000	2070	0.16
	53.6	0.206	0.94	31.0	66.5	VP ^d	0.076	0.388	1890	70	1090	2500	0.19
	54.6	0.156	1.08	30.5	77.8	1.03	0.398	1.000	1380	46	397	742	0.060
	54.6	0.156	1.08	30.5	77.8	1.03	0.398	1.000	1380	70	526	1420	0.11
	59.6	g	1.13	10.0	249	0.23	0.086	0.420	1990	46	910	1750	0.14
	59.6	8	1.13	10.0	249	0.23	0.086	0.420	1990	70	481	642	0.052
	59.6	8	1.13	10.0	249	0.79	0.086	0.420	2010	70	1520	8690	0.53
	59.6	g	1.13	10.0	249	0.79	0.086	0.420	2010	46	564	798	0.064
	60.4	8	1.19	30.8	85.3	0.26	0.087	0.408	1920	70	714	1150	0.092
	60.4	g	1.19	30.8	85.3	0.26	0.087	0.408	1920	70	877	1640	0.13
	60.4	8	1.19	30.8	85.3	0.26	0.087	0.408	1920	70	1250	3820	0.28
	60.4	g	1.19	30.8	85.3	0.26	0.087	0.408	1920	46	623	929	0.075
	60.4	g	1.19	30.8	249	VP ^d	0.087	0.408	1920	46	0	0	0

^a Unless noted otherwise, the temperature is 196 ± 1 K and the flow tube radius is 0.88 cm. ^bCalculated with the HCl mass excluded. ^cCalculated assuming a substrate density of 0.84 g/cm³. ^dVP indicates that no HCl was flowing into the reactor during the experiment and P(HCl) was presumably equal to the equilibrium partial pressure of HCl over the substrate. ^cTemperature equals 187 K. ^fWater frost from air leakage was observed upstream of the substrate; this may affect the accuracy of the measurement. ^gThe weight percent HCl was not measured; the extrapolated HCl saturation data indicate that it is probably below the limit of detectability.

Figure 3 shows a typical example of reactant and product signals vs time for reaction 2. To test for surface deactivation, a series of reaction probability measurements for reaction 2 were repeated over the same HNO₃-H₂O ice surface and are shown in Figure 4. The substrate used was 0.67 g of 45.6 wt % HNO₃. Over the 15-min duration of the experiment, γ_g decreased about 35%. The true γ_g (0.023) is determined from the intercept at zero reaction time. The difference between the true γ_g at zero time and the reaction probability (0.022) we obtained at short time is negligible. The data reported were not corrected for deactivation because the observed effect is much smaller than the correction for internal diffusion.

Table I summarizes the data for $CIONO_2 + H_2O$ reaction probabilities on HNO_3-H_2O ices. The results, after correcting for external and internal diffusion, are plotted vs substrate composition in Figure 5. A very sharp drop in reaction probability is observed over water-enriched NAT as the substrate composition approaches pure NAT. Reaction probabilities were not calculated from the rate of HOCl production by reaction 2 because the HOCl signal was generally much smaller than the CIONO₂ signal and because the reaction did not go to completion over the length of the substrate, making $S_t(\infty)$ difficult to determine. Only the first run on each substrate was used to calculate the reaction probability to minimize the effect of surface deactivation.

The HCl sticking coefficient on HNO_3-H_2O ice was also measured; it is plotted in Figure 6 and summarized in Table II. Figures 5 and 6 show that the HCl sticking coefficient and the probability of reaction 2 depend similarly on nitric acid composition. Some of the data near the composition of NAT listed in Table II were taken after an "induction" period of a few minutes. In these experiments the sticking coefficient increased by a factor of 5 or more after the induction period. This set of data represents about one-third of the HCl sticking coefficient measurements and is not as reliable as the rest of data. The cause of this "induction" is not understood, and future experiments using either X-ray diffraction or infrared absorption are planned to investigate this effect.

The experimental results for reaction 1 have been briefly discussed in a previous publication.⁷ Figures 7 and 8 show the observed reaction probabilities for reaction 1 on HNO_3-H_2O substrates; these results have been corrected for external diffusion only. The experimental results are also summarized in Table III. The reaction probabilities indicate that the reaction is uniformly fast for all substrate compositions. No surface deactivation effect was observed, and multiple runs on the same substrate are included in the results. Because the Cl₂ signal strength compares well to that of $CIONO_2$ and because the reaction reached completion within about 10 cm, Cl₂ production data as well as ClONO₂ decay data were used to calculate $k_s(obs)$. The fits to eq 7 yielded straight lines as they should for a first-order reaction. No statistically significant difference was observed in the reaction probabilities calculated from ClONO₂ decay or Cl₂ production. Because the results were uniform, within experimental error, for all the substrates, the data was first corrected for external diffusion and then averaged, giving 0.27 ± 0.04 (1 σ precision only). This value was then corrected for the substrate's effective surface area with use of an average value for the substrate thicknesses; the resulting average reaction probability is 0.1 ± 0.02 (1 σ precision only). Reaction probabilities greater than 0.1 are greatly influenced by external gas-phase diffusion; small differences in $k_s(obs)$ lead to large differences after correction for this effect. These large corrections explain some of the scatter in the data.

Whether the HCl continued to flow or not made no difference in the reaction probability except in the case of substrates of greater than 53.8 wt % HNO₃. In this case, no reaction was observed with the HCl valve closed because the small amount of HCl stored in the substrate is very rapidly depleted. At a concentration of 0.01 wt % HCl, a typical substrate mass of 1 g contains 9.0×10^{-8} mol of HCl/cm of substrate length. Typically, about 2.3×10^{-8} mol s⁻¹ of ClONO₂ enter the reactor, so for a reaction probability of 0.1, all the HCl from one cm of substrate is removed in about 40 s. This compares to the roughly 40 s needed to make a measurement at a given injector position. The results for high weight percent HNO₃ ices with no HCl flow are not included in the average nor plotted in the figures.

The reaction probability of HCl with ClONO₂ was also measured in the reactor with no substrate present. The reaction probability, corrected for external gas-phase diffusion, was found to be about 0.02–0.04 for HCl partial pressures in the range 0.2–20 mTorr. The homogeneous bimolecular gas-phase reaction is very slow at room temperature,^{22,23} and the lack of an HCl pressure dependence in the uncoated reactor indicates that the gas-phase reaction is also slow compared to the surface reaction at 196 K. The possible effect of the glass reactor wall was ignored in calculating the reaction probability for reaction 1, as it is a small effect. The effect of reaction 2 was also ignored because the maximum measured reaction probabilities for this reaction are only about 0.002 after correcting for the effective surface area.

Discussion

The substrate may be a two-phase mixture over some of the composition range covered in the experiments as suggested by the infrared absorption spectra discussed above. For two solid phases comprising NAT and H_2O ice, a model can be constructed in which the overall reaction probability is the sum of two components

$$\gamma_2 = a_{\rm I} \gamma_{\rm I} + a_{\rm NAT} \gamma_{\rm NAT} \tag{9}$$

where γ_1 is the reaction probability on the ice phase, γ_{NAT} is the reaction probability on the NAT phase, a_1 is the ice fraction of the total surface area, and a_{NAT} is the NAT fraction of the total surface area.

Assuming that we have pure NAT at 53.8 wt % HNO₃, then on the H₂O-rich side of NAT, the mass fraction of the ice phase (w(ice)) is given by

$$w(ice) = 1 - 1.86w(HNO_3)$$
 (10)

where $w(HNO_3)$ is the substrate's mass fraction of HNO₃. The relationship between w(ice) and the ice surface area depends on the structure of the two-phase substrate. Figure 5 shows a plot of γ_2 predicted by eq 9 for different γ_1 s compared to the experimental data assuming that a_1 is equal to w(ice) and that a_{NAT} is equal to w(NAT), with γ_{NAT} taken to be 1×10^{-5} . It can be



Figure 9. Comparison of time constants for HCl adsorption, the $CIONO_2$ + HCl reaction, and the $CIONO_2$ + H₂O reaction in the polar stratosphere. See text for detail.

seen that although the predicted γ_2 drops quite sharply near the trihydrate composition, it does not match the experimentally determined γ_2 , which begins decreasing at a smaller weight percent HNO₃.

Figure 6 shows a similar plot for a two-phase model, identical with the γ_2 model above, compared to the experimentally determined HCl sticking coefficients. As was the case for the γ_2 model, the observed reaction probability as a function of substrate composition drops at a lower weight percent HNO₃ than predicted by the model. The ternary HCl/HNO₃/H₂O system is an added complication in evaluating models of the HCl sticking coefficient.

The best least-square fits of our data shown in Figures 5 and 6 give $\gamma_1 = 0.005$ for reaction 2 and $\gamma_1 = 0.04$ for the HCl sticking coefficient. These values are much smaller than our previous data of 0.06 for reaction 2 and 0.4 for the HCl sticking coefficient,⁵ which are not corrected for the internal surface area. In another study¹⁹ we found that the H₂O ice is also porous and the correction for this effect is also required.

To rigorously evaluate this model, a precise knowledge of how a_i and a_{NAT} vary with substrate composition is necessary. These data are not available, and the above models can be viewed as only semiquantitatively describing our experimental results.

There are several measurements of ClONO₂ and HCl on H_2O ice^{5,24,27} and H_2SO_4 .^{26,28} Comparison with our present data on

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 HNO_3 - H_2O ice is not possible. However, during the preparation of this paper we received a preprint from Hanson and Ravishankara²⁸ who found the reaction probabilities of $\gamma_1 = 0.3$ for the ClONO₂ + HCl reaction and of $\gamma_2 = 0.006$ for the ClONO₂ + H₂O reaction on a "NAT" surface that was prepared by reacting ClONO₂ with H₂O ice at 200 K and allowing the HNO₃ product to build up in the substrate. The surface area and the bulk density of their substrate were not measured. The HNO₃-covered H₂O ice was assumed to be nonporous. Their value of $\gamma_1 = 0.3$ is in excellent agreement with our value of 0.27 prior to correcting for internal surface area. If we correct their data for internal surface area by using our measurements of porosity and BET surface area and an estimated average ice thickness of 11 μ m in their work, we obtain $\gamma_1 = 0.2$, which is a factor of 2 larger than our corrected value of 0.1 ± 0.02 . After correction for the internal diffusion, their value for γ_2 becomes 0.002. Hanson and Ravishankara argue that their "NAT" surface may be about 48-52 wt % HNO₃ by referring to the HNO₃ partial vapor pressure measurement by Hanson and Mauersberger.¹⁸ If we assume their "NAT" surface is about 48 wt %, γ_2 would be a factor 2 greater than our data shown in Figure 8. These differences are not significant in view of the difficulties associated with the reaction probability measurements.

To our knowledge there is no previous measurement of the HCl sticking coefficient on type I PSCs. Thus, our result represents the first determination.

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The possible effect of our preliminary results on calculated ozone loss in the polar stratosphere has been discussed briefly.⁷ Time constants for heterogeneous processes on PSCs as suggested by Turco et al.⁴ are given by

$$t = 4/\gamma\omega S \tag{11}$$

where γ is the HCl sticking coefficient or ClONO₂ reaction probability, ω is the molecular velocity of HCl or ClONO₂, and S is the surface area of type I PSCs per unit volume. For these calculations, we assume S to be 1×10^{-7} cm²/cm³ for fully developed PSCs³ and use the measured γ s for HCl adsorption and for reactions 1 and 2. The results are shown in Figure 9. A typical lifetime of a PSC is about a few days (approximately 106 s).⁴ The time constant for HCl adsorption ranges from 1×10^5 s at 40 wt % HNO₃ to about 2×10^7 s at 54 wt %. This suggests that only PSCs composed of H₂O-rich NAT could readily incorporate HCl. The heterogeneous chemical process responsible for converting inactive chlorine to active forms is the CIONO₂ + HCl \rightarrow Cl₂ + HNO₃ reaction. The time constant for this process is about a few hours. Finally, it should be noted that the $CIONO_2 + H_2O \rightarrow HOCI + HNO_3$ reaction on type I PSCs is probably too slow to play a role in the polar stratosphere.

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Registry No. CIONO₂, 14545-72-3; HCl, 7647-01-0.

Adsorption of Acetylene on Rhodium- or Platinum-Modified Silver and Gold Electrodes: A Surface-Enhanced Raman Study

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Surface-enhanced Raman spectra (SERS) of acetylene adsorbed on rhodium- and platinum-modified silver and on rhodium-modified gold were determined at room temperature in both acidic and neutral supporting electrolytes. In acidic media the spectra exhibited intense bands in the vicinity of 1100 and 1500 cm⁻¹; similar peaks were observed on unmodified gold, but not on unmodified silver. In a neutral environment the same bands appeared on rhodium-modified gold, and sometimes on unmodified gold; they were never detected on silver or on silver modified by transition metals. The 1100- and 1500-cm⁻¹ bands were assigned to sp² or sp³ rehybridized forms of acetylene, possibly produced by catalytic hydrogenation on the surface of the electrodes. Their intensities reversibly increased at negative potentials, suggesting a potential related formation and desorption of the new species. Weak bands, attributed to unhybridized acetylene molecules $\sigma\pi$ -bonded to the surfaces, were occasionally observed in the 1800-2300-cm⁻¹ spectral region. No signals appeared on polished electrodes, even when these were modified by thin layers of rhodium or platinum, and the intensity of the peaks decreased gradually when increasing amounts of transition metal were deposited on the roughened substrates. The bands were therefore ascribed to surface enhancement phenomena rather than to bulk Raman scattering.

Introduction

The surface chemistry of acetylene adsorbed onto transition metals has been the subject of intensive investigation, albeit with rather contradictory results. Studies by normal Raman (NR) and surface-enhanced Raman spectroscopy (SERS), both in ultrahigh vacuum at various temperatures¹⁻⁵ and in electrochemical systems,⁶ indicate that while the adsorbed acetylene undergoes various degrees of rehybridization, the molecule remains essentially whole.¹⁻⁴ Polymerization on the surface has sometimes been

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