

A KINETICS STUDY OF THE HOMOGENEOUS AND HETEROGENEOUS COMPONENTS OF THE HCl + ClONO₂ REACTIONRandall R. Friedl, James H. Goble¹ and Stanley P. Sander

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Abstract. The kinetics of the reaction $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$ were investigated at 298 K using a flow reactor with FTIR analysis to assess the importance of this reaction for stratospheric chemistry. The observed reaction was characteristic of a heterogeneous process; an upper limit of $5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained for the homogeneous gas phase rate constant. From calculations of the first order wall rate constant, estimates were made of the reaction rate on stratospheric aerosols. Because both HCl and ClONO₂ need to be adsorbed on the particle surface, the reaction will be of negligible importance under most stratospheric conditions.

Introduction

Considerable interest has been focused recently on homogeneous and heterogeneous reactions between temporary reservoir species in the stratosphere [DeMore et al., 1985; WMO, 1986]. One such reaction,



has received particular attention because of its large potential impact on the odd chlorine (ClO_x) budget even at relatively small values of the gas-phase reaction rate coefficient ($k_1 > 5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [Prather et al., 1984; WMO, 1986]. Laboratory studies of this reaction using flow systems [Birks et al., 1977; Molina et al., 1985] have indicated the presence of a wall-catalyzed component. If the reaction is carried out under conditions which minimize the role of the reactor walls, as in the study of Molina et al. [1985], a very small upper limit ($k_1 < 1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is obtained for the gas phase component of reaction 1, ruling out any potential stratospheric role for the homogeneous reaction.

The importance of the surface-catalyzed reaction in the stratosphere is more difficult to estimate. Ordinarily, the surface area of the middle stratospheric aerosol is too small for surface reactions of radicals to compete with gas phase processes [WMO, 1986]. Processes which are extremely slow in the gas phase, such as the reactions of N₂O₅ and ClONO₂ with H₂O, H₂O₂ and HCl, may be enhanced by interactions with surfaces, most notably when the aerosol loading is increased by a mechanism such as volcanic injection or the formation of polar stratospheric clouds. In particular, Solomon et al. [1986] have suggested that the occurrence of reaction 1 on

polar aerosols at an equivalent bimolecular rate of $2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ can help explain the remarkable depletions in the total ozone content in Antarctica during the springtime.

In this study, a flow system was used with FTIR analysis to obtain estimates of both the homogeneous and heterogeneous contributions to the rate of the HCl + ClONO₂ reaction. Calculated wall reaction rates were extrapolated to stratospheric conditions to obtain lifetimes for the conversion of ClONO₂ to active chlorine by reaction 1. It is shown that, even under the most favorable conditions, it is unlikely that the heterogeneous reaction of HCl with ClONO₂ will be an important process in the stratosphere.

Experimental

The flow reactor consisted of a 6 in. diameter Pyrex tube coupled to a 650 cfm Roots blower backed by a 150 cfm mechanical pump. The reactor could also be exhausted to a fume hood for atmospheric pressure operation. The inside surface of the tube was coated with Teflon (DuPont 856-200). The optical system consisted of a Bomem DA3.002 Fourier Transform Infrared spectrometer coupled to White-type optics in the flow tube (150 cm base path, 40 m path length) and a liquid helium-cooled Cu:Ge detector using cooled infrared interference filters.

Kinetic runs were carried out over the pressure range 1 - 730 torr of helium or nitrogen diluent using a flow velocity of 10 cm s⁻¹. HCl flowed either from a premixed bulb or directly from the cylinder through an electronic mass flowmeter before entering the flow tube. ClONO₂ was obtained by flowing a portion of the carrier gas through a bubbler containing liquid ClONO₂ at -78 C. The reagents could be premixed in a short 15 cm long, 5 cm dia. section upstream of the main flow tube, or in the flow tube itself by adding the ClONO₂ through a sliding injector positioned along the flow tube axis. The reaction conditions were such that HCl was generally in great excess over ClONO₂. HCl concentrations ranged from 5×10^{13} to $1 \times 10^{18} \text{ molecule cm}^{-3}$. ClONO₂ concentrations varied from 1 to $20 \times 10^{13} \text{ molecule cm}^{-3}$. Reactants and products were analyzed from FTIR scans taken at 0.1 cm⁻¹ resolution. ClONO₂ was monitored in the ν₂ band (NO₂ symmetric stretch) at 1290 cm⁻¹ while HNO₃ was monitored in the ν₄ band (NO₂ symmetric stretch) at 1325 cm⁻¹. Infrared absorbances for HNO₃ and ClONO₂ were calibrated against UV spectrometric and barometric measurements, respectively.

Results

Experiments were carried out by fixing the flow rate of ClONO₂ at a given total pressure of diluent gas and measuring the integrated ClONO₂ band absorption before and after the addition of HCl. With HCl present, ClONO₂ disappearance and

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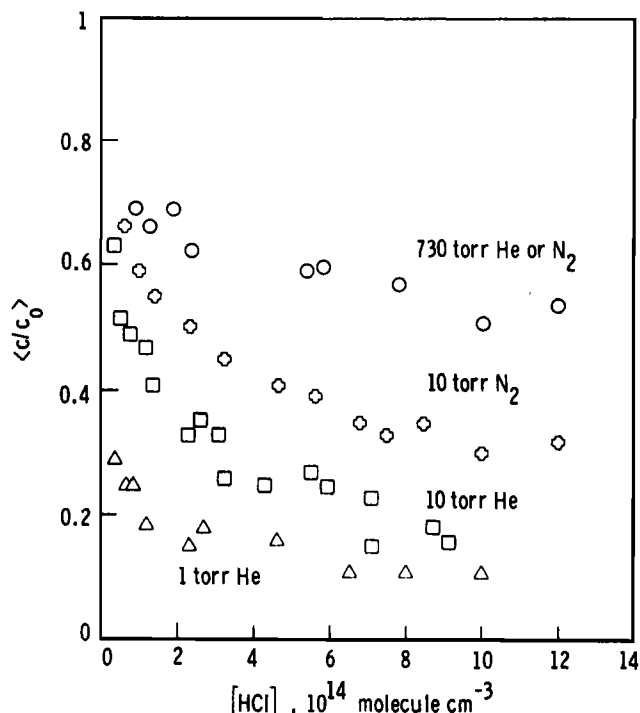


Fig. 1. Pressure dependence of the integrated ClONO₂ depletion vs. [HCl].

HNO₃ formation were observed. Since the optical system integrates the ClONO₂ absorption along the flow tube axis, the measured depletion is given by

$$\langle c/c_0 \rangle = \frac{1}{[ClONO_2]_0 l} \int_0^l [ClONO_2] dz \quad (2)$$

The dependence of $\langle c/c_0 \rangle$ on [HCl] is shown in Figures 1 and 2. From Figure 1, it is apparent that ClONO₂ is quickly depleted with the addition of even the lowest concentrations of HCl but that this removal quickly saturates with increasing HCl. Figure 2 shows the dependence of $\langle c/c_0 \rangle$ on [HCl] over the range 1×10^{14} to 1×10^{18} molecule cm⁻³ at 1 atm. total pressure of N₂. Above HCl concentrations of 2×10^{14} molecule cm⁻³ the dependence of $\langle c/c_0 \rangle$ on [HCl] is weak and the presence of high (30 torr) pressures of HCl does not completely remove the chlorine nitrate, which is present in concentrations about five orders of magnitude below the HCl. From the data in Figure 2, an upper limit of about 5×10^{-18} cm³ molecule⁻¹ s⁻¹ can be derived for the homogeneous (gas phase) component of reaction 1. The data in Figure 1 also indicate that the global reaction rate shows a pronounced inverse pressure dependence, i.e. increasing diluent gas pressure causes a decrease in rate. Under conditions of constant reactor residence time (15 s), [ClONO₂]₀ (2×10^{-13} molecule cm⁻³) and temperature (298 K), reactivity increases as total pressure decreases in the following order: 730 torr He or N₂, 10 torr N₂, 10 torr He, 1 torr He.

As indicated in Figure 1, kinetic runs carried out under the same conditions produced repeatable results, indicating that the reactivity and adsorption/desorption characteristics of the reactor walls were stable. At each pressure, the quantity [ClONO₂] + [HNO₃] was constant. This indicates a) that the total concentration of reactive nitrogen in the system is conserved, b)

that no important product channels have been overlooked and c) that there is no heterogeneous loss of reactive nitrogen.

To better characterize the system, several variations of the ClONO₂ depletion experiment were carried out. As a qualitative check on the reactivity of the walls, several runs were performed at 10 torr He with the flow tube lined with 0.5 mm thick TFE Teflon sheet. The use of this material resulted in more rapid ClONO₂ removal than under the corresponding conditions with the Teflon coating. Several runs were carried out using the flow tube injector to introduce the ClONO₂ several centimeters downstream from the main carrier gas injection point, the objective being to ensure that the flow was laminar before the chemical reaction could begin. Variation of the injector position had no effect on the overall reaction rate.

Discussion

Three features of the kinetic data strongly suggest that the HCl + ClONO₂ reaction is a wall-catalyzed process in this system: 1) the dependence of ClONO₂ depletion on added HCl, which is characteristic of an adsorption isotherm, 2) the inverse dependence of the ClONO₂ depletion upon total pressure and 3) the sensitivity of the reaction rate to the wall material. Some insight into the origin of these features can be obtained by considering the details of the simultaneous processes of diffusion and reaction in the flow tube.

For the bimolecular reaction taking place under pseudo-first order conditions in the gas phase, the observed loss of ClONO₂ is given by

$$\langle c/c_0 \rangle = \frac{v}{k_1 [HCl] l} \left(1 - e^{-k_1 [HCl] l/v} \right) g(R) \quad (3)$$

where $\langle c/c_0 \rangle$ = reactant depletion observed by integrating along a tube of length l , k_1 = bimolecular rate constant for the gas phase reaction, v = flow velocity, $g(R)$ = radial concentration distribution function. The function $g(R)$ allows for the fact that the optical system samples uniformly across the tube radius and ClONO₂ will, in general, not have a uniform radial distribution due to wall reaction and radial and axial diffusion. For pressures in the 1-10 torr regime, $g(R)$ may be assumed to be unity. Under these conditions, it was found that the above relationship could not be fit to the observed dependence of $\langle c/c_0 \rangle$ on [HCl] suggesting that the

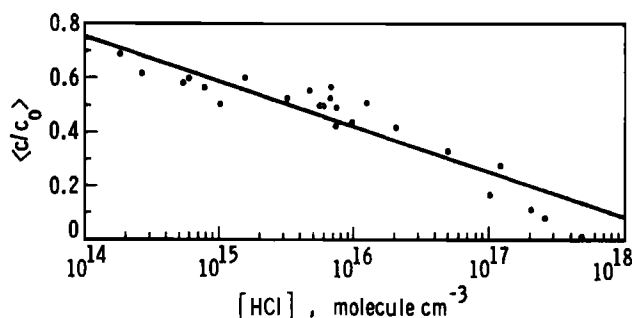


Fig. 2. Integrated ClONO₂ depletion vs. [HCl] at 1 atm. total pressure of N₂.

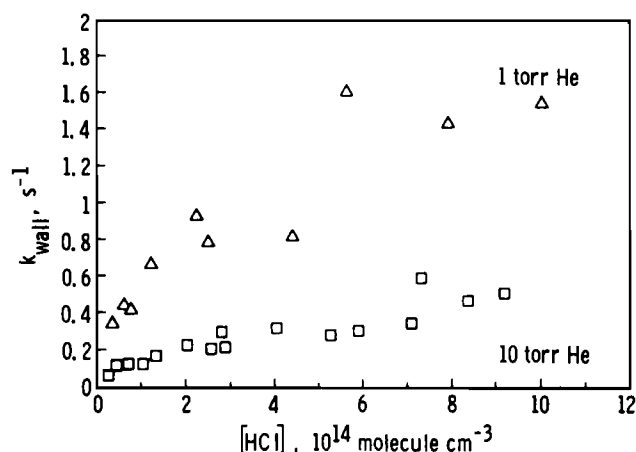


Fig. 3. Pressure dependence of the pseudo first-order wall reaction rate constant, k_{wall} , vs. $[\text{HCl}]$ computed using the assumption that the homogeneous component of the HCl + ClONO₂ reaction is negligible.

reaction did not proceed by a direct homogeneous gas-phase process.

In order to more fully understand the effects of diffusion and wall reaction, the continuity equation for fully developed laminar steady state tube flow was applied using the solution of Walker [1961] and the computer algorithm of Brown [1978]. The results of the flow tube modelling calculations are shown in Figure 3. The wall rate constant, k_w , has both a pressure dependence between 1 and 10 torr and a nonlinear dependence on $[\text{HCl}]$ over the range $(0.2-10) \times 10^{14}$ molecule cm^{-3} . A dependence on the HCl concentration is expected based upon the assumption that reaction 1 is a heterogeneous process whose rate depends on the density of reactive surface sites occupied by HCl. The nonlinear dependence on $[\text{HCl}]$ indicates that the surface adsorption isotherm of HCl is approaching saturation in this concentration range. The data at both 1 and 10 torr He suggest that the linear portion of the isotherm would manifest itself at HCl concentrations below about 1×10^{13} molecule cm^{-3} .

The computed values of k_w display an inverse pressure dependence, decreasing by about a factor of 4 between 1 and 10 torr of helium. A similar effect was observed by Loewenstein and Anderson [1985] who studied the pressure dependence of the reactions of OH radicals with I₂ and ICl in a discharge flow reactor between 1 and 10 torr of He and Ar. They suggested that the diluent gas itself might have exerted a direct effect on k_w by occupying some of the active sites. In this study, the reactor surface is not sufficiently well characterized to model the wall reaction in detail. In addition, because of the slow flow velocity (10 cm s⁻¹), axial diffusion is very important in the 1 torr experiments, and the large correction entailed by this effect also complicates the interpretation of the experiments at this pressure. The results for k_w at 10 torr helium should be somewhat more reliable as the corrections for both radial and axial diffusion are less than 20 per cent under these conditions.

Previous studies of reaction 1 have employed a variety of reactor types which differ in such characteristics as total pressure, gaseous transport rate, and surface to volume ratio.

Since these reactor characteristics determine the sensitivity of the reactors to wall catalyzed processes, they can account for the large differences in the previously reported upper limits for k_1 : Birks et al. [1977] ($k_1 \leq 1.2 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, measured in fast-flow apparatus); Molina et al. [1985] ($k_1 \leq 1 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹, pulsed jet); Hatakeyama and Leu [1986] ($k_1 \leq 8.4 \times 10^{-21}$ cm³ molecule⁻¹ s⁻¹, static photolysis); this work ($k_1 \leq 5 \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹, slow-flow).

Implications for Stratospheric Chemistry

The upper limits to the value of k_1 measured by Molina et al. [1985], Hatakeyama and Leu [1986] and ourselves rule out the possibility of a significant regeneration of active chlorine through this reaction in the gas phase. However, the possibility remains that the reaction can take place heterogeneously on the surface of stratospheric aerosols. The measurement in this study of k_w as a function of the gas phase HCl concentration permits an estimate to be made of the stratospheric lifetime of ClONO₂ under assumed conditions of stratospheric aerosol loading. Such a calculation is necessarily very approximate because of large uncertainties in the size distribution and catalytic efficiency of the aerosol. There will also be differences between the adsorption isotherms and reactivities of the aerosol and the Teflon wall coating of the laboratory reactor. Nevertheless, an order-of-magnitude estimate will be instructive.

The pseudo-first order rate constant for the disappearance of ClONO₂ in the presence of an HCl-coated surface is given by

$$k_w = k_{\text{coll}} \gamma \quad (4)$$

where k_{coll} is the first order collision rate with the surface and γ is the reactive collision efficiency. For particles larger than the mean free path, k_{coll} will be proportional to the aerosol surface area per unit volume. γ is a function of both the surface HCl concentration and the intrinsic catalytic properties of the substrate. In the linear portion of the adsorption isotherm, the surface HCl concentration will be proportional to $[\text{HCl}]$. In the laboratory system, this regime is encountered under conditions where $[\text{HCl}] < 1 \times 10^{13}$ molecule cm^{-3} , as indicated in Figure 2. If it is assumed that Teflon and atmospheric aerosol surfaces have equivalent adsorption isotherms and catalytic properties, the first order heterogeneous rate constant for ClONO₂ removal by HCl in the stratosphere is given by

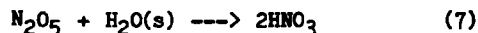
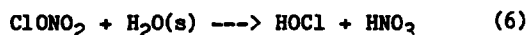
$$k_w^{\text{atm}} = k_w^{\text{lab}} \frac{S_{\text{atm}} [\text{HCl}]_{\text{atm}}}{S_{\text{lab}} [\text{HCl}]_{\text{lab}}} \quad (5)$$

where k_w^{lab} (0.1 s⁻¹) is the observed laboratory rate constant at the reference HCl concentration, S_{atm} and S_{lab} are the volumetric surface areas of the atmospheric aerosol and the laboratory reactor, respectively, $[\text{HCl}]_{\text{atm}}$ is the stratospheric HCl number density (10^9 molecule cm^{-3}) and $[\text{HCl}]_{\text{lab}}$ is the laboratory reference HCl concentration (10^{13} molecule cm^{-3}). Using a liberal estimate for the surface area of a stratospheric aerosol, $1000 \mu^2 \text{cm}^{-3}$ [Hofmann and Rosen, 1985], and a value of $2.6 \times 10^7 \mu^2 \text{cm}^{-3}$ for

S_{lab} , eqn. (5) gives a value of $4 \times 10^{-10} \text{ s}^{-1}$ for k_w^{atm} , or a lifetime greater than 1000 years. For comparison with the calculations of Solomon et al. [1986], an equivalent bimolecular rate constant for the heterogeneous reaction of $4 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ can be derived from k_w^{atm} . This bimolecular rate constant is nearly five orders of magnitude smaller than the value required by Solomon et al.

The major uncertainty in this calculation has to do with the extrapolation of γ from the laboratory case to the stratospheric situation. At the lower atmospheric temperatures, the adsorption isotherm of HCl will probably shift in the direction of higher surface HCl concentrations, however, the temperature dependence of the rate of surface catalysis is unknown. Overall, the HCl + ClONO₂ reaction does not appear to have a large temperature dependence; Molina et al. [1985] observed an increase in k_w^{lab} of less than a factor of 2 as the temperature was decreased from 294 K to 241 K.

While very approximate, this calculation suggests that the HCl + ClONO₂ reaction will be three to four orders of magnitude too slow to cause any significant conversion of reservoir chlorine to the more labile form, Cl₂, on a time scale comparable to other reactions of HCl. The reason for this is that both reactants, which are present in trace concentrations in the gas phase, must be adsorbed onto the surface before reaction can take place. In contrast, reactions which take place on aqueous surfaces such as



can proceed considerably faster since the surface substrate plays a role as a chemical reactant.

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