An Upper Limit to the Rate of the HCl + ClONO₂ Reaction

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The reaction $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$ has been studied by FTIR spectroscopy and by a static wallless UV absorption technique. An upper limit to the homogeneous bimolecular rate constant of 10^{-19} cm³ molecule⁻¹ s⁻¹ was established, making the reaction unimportant in the stratosphere.

Introduction

The reaction between HCl and $ClONO_2$ is potentially a very important component of stratospheric chemistry.[1] The reactants are the two most abundant temporary chlorine-reservoir species, and the net effect of the reaction is to return chlorine to its active form as a catalyst for ozone destruction, since the product Cl_2 photolyzes rapidly in the stratosphere yielding free chlorine atoms:

$$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2, \quad \Delta H = -16.5 \text{ kcal/mol} \tag{1}$$

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{2}$$
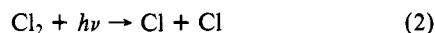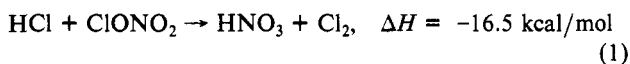
The only published study[2] of reaction 1 reports an upper limit for the rate constant of 1.2×10^{-15} cm³ molecule⁻¹ s⁻¹; such a value would imply that the reactions of HCl with $ClONO_2$ and with OH proceed at comparable rates in the lower stratosphere (OH attack is the predominant HCl destruction mechanism). In fact, even a rate constant as small as 10^{-17} cm³ molecule⁻¹ s⁻¹ would have a significant impact on ozone depletion estimates,[3] particularly for high chlorine scenarios.[4]

Stratospheric chemistry is dominated by fast reactions involving free-radical species and by photochemical processes, and bimolecular reactions between nonradical molecules have been assumed to occur at negligible rates at stratospheric temperatures.[5] However, the theoretical framework in chemical kinetics behind this assumption is not sufficiently firm to rule out all such reactions. Furthermore, exceptions exist which can be rationalized theoretically, such as the very fast $NaOH + HCl \rightarrow NaCl + H_2O$ reaction[6] which appears to proceed through the formation of an intermediate with ionic character. Other examples of such fast processes are $KI + CsCl \rightarrow CsI + KCl$ and $CsI + Cl_2 \rightarrow CsCl + ICl$ (four center),[7] and $Br_2 + (Cl_2)_2 \rightarrow 2 BrCl + Cl_2$ (six center).[8] The $ClONO_2$ molecule is polar, the chlorine being "functionally electropositive", hence the name "chlorine nitrate".[9] It appears plausible, then, for the HCl + $ClONO_2$ reaction to be reasonably fast if one considers the ionic character of the reactants; in fact, it has been reported as a fast reaction at −90 °C in CCl_4 solution.[10]

We have studied reaction 1 in 1 atm of Ar, using (1) FTIR spectroscopy coupled to a flow system and (2) a novel static wallless technique with UV absorption spectroscopy. We determined an upper limit for the gas-phase rate constant which makes it unimportant as a homogeneous process in the stratosphere.

Experimental Section

Steady-State Flow Infrared Absorption Apparatus. A schematic of the apparatus is shown in Figure 1. A Nicolet 20SX Fourier transform infrared spectrometer (FTIR) equipped with a liquid-nitrogen-cooled HgCdTe detector was interfaced to a Teflon-coated, jacketed cell, 60 cm long and 5 cm in diameter. The cell was fitted with internal mirrors in a "White" optics arrangement, providing an optical absorption path of ~20 m.

Methanol was circulated through the jacket for temperature control (230–295 K). The $ClONO_2$/Ar flow was rapidly mixed with the main HCl/Ar flow at the entrance of the cell by a multiple-orifice injector. The reactant concentrations were measured continuously by UV absorption spectrophotometry. The FTIR spectra were recorded at 1-cm⁻¹ resolution.

Static, Wallless Reaction Cell. Figure 2 shows a schematic of the apparatus. A 60 cm long, 12 cm in diameter glass cylinder was fitted with an injector tube attached to a Teflon solenoid valve which could be opened for preselected time intervals. For most experiments the cell was filled with 730 torr of Ar mixed with HCl in the 0–2 torr range. The gas mixture to be injected into the absorption cell ($ClONO_2$ or Cl_2 in Ar) was kept in a 200-cm³ glass container attached to the solenoid valve; typically, the solenoid valve was activated for a 10-ms period which resulted in a pressure drop in the glass container from 900 to 895 torr.

The absorption cell was fitted with "White" optics using internal, Al-coated mirrors and providing an optical path length of ~10 m. The probe light was supplied by a 75-W high-pressure Xe arc lamp and was focussed onto a photodiode after traversing the cell and passing through a 7-60 Corning glass filter, whose transmission curve overlaps with the Cl_2 absorption band at 330 nm, a spectral region where absorption by $ClONO_2$, HNO_3, and HCl is negligible. The photodiode signal was recorded on a Nicolet 1170 signal averager. A second, single-pass probe beam employed a Hg lamp–dielectric filter–solar blind photomultiplier arrangement to monitor absorbance at 185 nm; it was used to measure the initial HCl concentration in the absorption cell.

Chemicals. HCl, Cl_2, NO_2, NO (Matheson Gas Products) and Ar (MVE Cryogenics) were used without further purification. All gases were handled on a greaseless glass–Teflon vacuum line equipped with MKS capacitance manometers and Matheson mass flow meters. Chlorine nitrate was synthetized from Cl_2O and N_2O_5 as described previously.[11]

Results and Discussion

FTIR Experiments. The FTIR spectra of the flowing HCl/

(1) Rowland, F. S., presented at the International Meeting on Current Issues in our Understanding of the Stratosphere and the Future of the Ozone Layer, Feldafing, West Germany, June 11–16, 1984.

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(8) Dixon, D. A.; Herschbach, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 6268.

(9) Schmeisser, M.; Braendle, K. *Angew. Chem.* **1961**, *73*, 388.

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(11) Molina, L. T.; Spencer, J. E.; Molina, M. J. *Chem. Phys. Lett.* **1977**, *45*, 158.
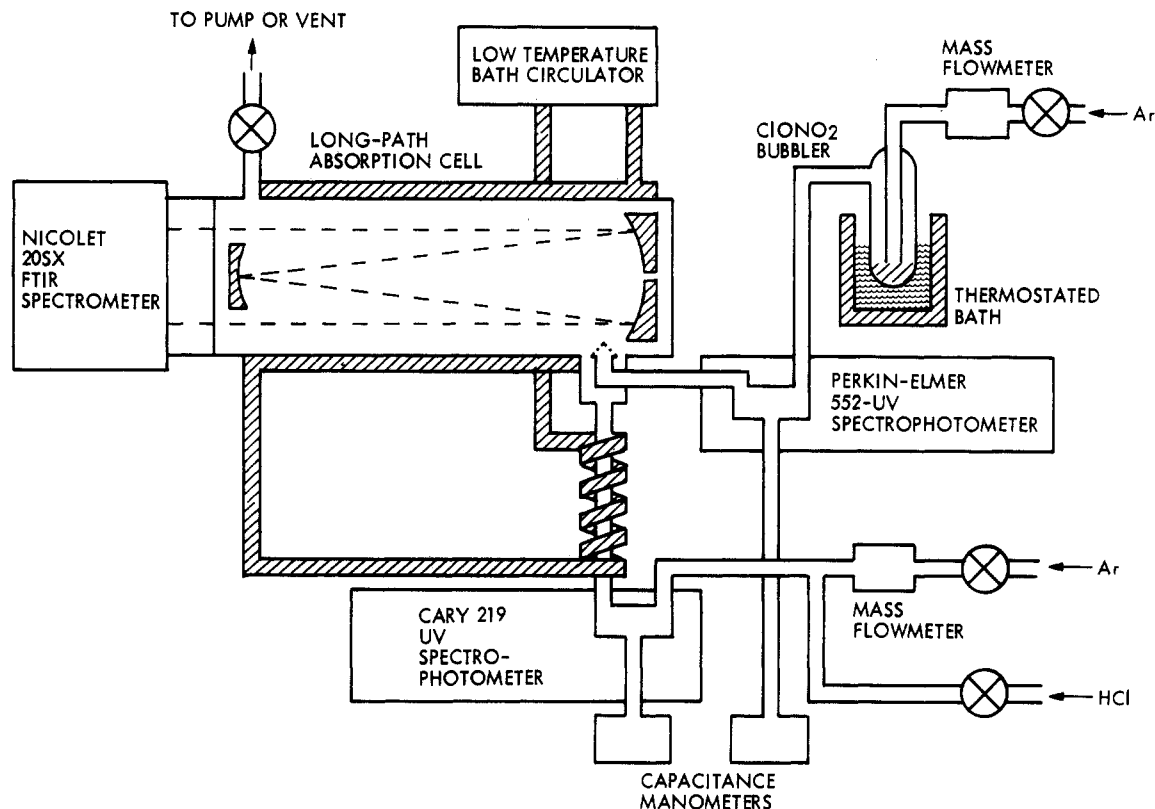
[†]NASA/NRC Resident Research Associate.

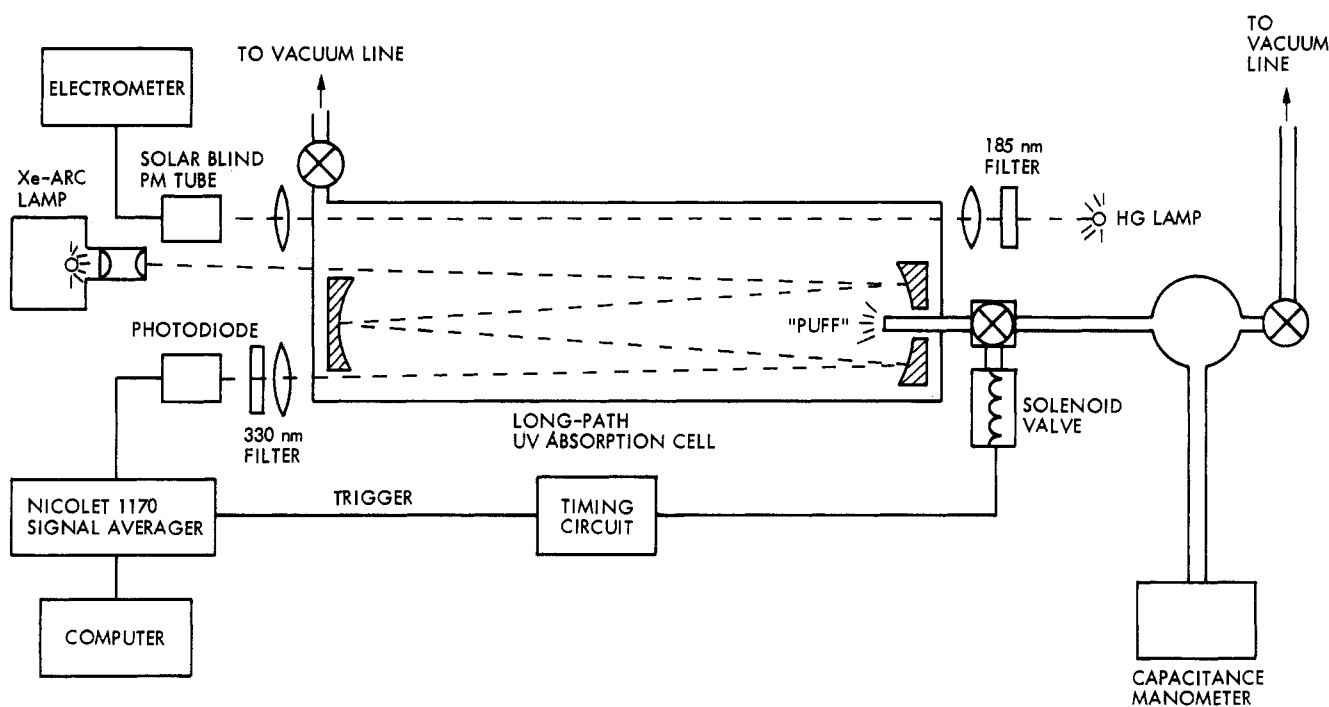**Figure 1.** Schematic diagram of the steady-state flow FTIR apparatus.

Figure 2. Schematic diagram of the static wallless long-path UV absorption apparatus.

$ClONO_2$/Ar mixtures indicate that reaction 1 does take place in the Teflon-coated absorption cell: HNO_3 was formed in amounts corresponding to the observed decrease in $ClONO_2$, and only the known IR bands belonging to HCl, $ClONO_2$, and HNO_3 appeared in the spectra.

The $ClONO_2$ concentration is expected to decrease exponentially along the cell if one assumes reaction 1 to occur in the FTIR cell as an elementary gas-phase bimolecular process, since HCl was in large excess (pseudo-first-order conditions). Hence, apparent bimolecular rate constants k^{II} could be computed as a function of the residence time, t, the concentration of the excess reactant, [HCl], the chlorine nitrate concentration averaged along

the cell and sampled through its infrared absorbance, $[ClONO_2]_{av}$, and the chlorine nitrate concentration at the cell entrance, $[ClONO_2]_0$:

$$[ClONO_2]_{av} = \frac{[ClONO_2]_0}{k^{II}[HCl]t} \{1 - \exp(-k^{II}[HCl]t)\}$$

The k^{II} values determined with this equation were nearly temperature independent and ranged from $\sim 10^{-16}$ cm^3 molecule^{-1} s^{-1} for $t = 0.8$ s and [HCl] = 10^{15} molecule cm^{-3}, to about 10^{-18} cm^3 molecule^{-1} s^{-1} for $t = 14$ s and [HCl] = 5×10^{16} molecule cm^{-3}. These k^{II} values were not sensitive to the $ClONO_2$ con-
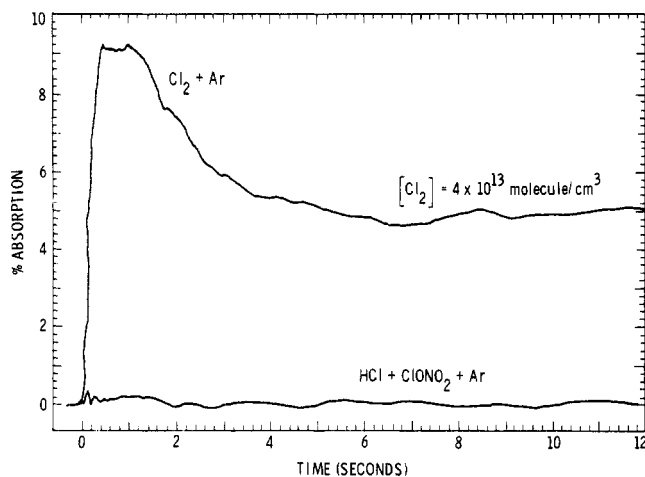
Figure 3. Typical Cl_2 absorption profiles. Upper trace: injection of Cl_2 into 730 torr of Ar; lower trace: injection of $ClONO_2$ into 730 torr of Ar mixed with 1.1 torr of HCl. The amount of $ClONO_2$ injected is the same as the amount of Cl_2 injected for the upper trace.

centration, which ranged between 5×10^{13} molecule cm^{-3} and 10^{15} molecule cm^{-3}.

An upper limit to the homogeneous gas-phase bimolecular rate constant of $\sim 10^{-18}$ cm^3 molecule^{-1} s^{-1} can be inferred from these experiments under the assumption that surface processes are responsible for the larger k^{II} values; the rate constant for the elementary gas-phase process should be, of course, independent of [HCl] and of t. However, other assumptions are feasible, namely more complicated homogeneous gas-phase mechanisms such as:

$$HCl + ClONO_2 \rightarrow I$$

$$I \rightarrow Cl_2 + HNO_3$$

$$HCl + I \rightarrow 2HCl + ClONO_2$$
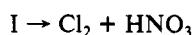
with a small steady-state concentration of the intermediate I to allow for the fact that no unidentified IR bands appeared in the spectra.

Static Cell Experiments. Figure 3 (upper trace) shows a typical concentration–time profile due to injection of a Cl_2/Ar mixture into the absorption cell resulting in a final Cl_2 concentration of 4×10^{14} molecule cm^{-3}. The shape of the signal is determined by the evolution of the injected Cl_2/Ar "puff" and its overlap with the optical probe beam.

Control experiments, monitored with a video camera, in which NO_2/Ar mixtures were released into ~ 1 atm of Ar in the absorption cell established that the injected samples or "puffs" did not reach the container walls for periods of 2–3 s. Furthermore, injection of O_2/Ar mixtures into 1 atm of NO produced optical absorption signals indistinguishable, within experimental error, from those shown in the upper trace of Figure 3, the probe light being absorbed by NO_2 produced by the $2NO + O_2$ reaction. Hence, mixing of the reactants occurs on a time scale which is short in comparison with the initial appearance of the absorption signal (~ 0.5 s).

Figure 3 also shows a typical signal resulting from injection of a $ClONO_2/Ar$ mixture into the cell containing 730 torr of Ar and 1.1 torr of HCl (lower trace). Clearly, no measurable amount of Cl_2 is formed in the first few seconds, the expected Cl_2 signal appearing only after tens of seconds. Similar results were obtained for HCl concentrations in the 0.2–2-torr range.

There are no exothermic channels to the HCl + $ClONO_2$ reaction other than the one yielding Cl_2 and HNO_3 (reaction 1), except possibly for the channel producing an HCl–$ClONO_2$ adduct which was, however, not observed in the FTIR experiments, even at 230 K. Hence, a conservative upper limit to the reaction between HCl and $ClONO_2$ of 10^{-19} cm^3 molecule^{-1} s^{-1} can be set by considering the base line noise and the absorption signals due to Cl_2 injection. This upper limit is consistent with the FTIR results, and we conclude that a Teflon surface is an efficient catalyst for reaction 1. The occurrence of this reaction has been noted by other investigators as well, with results that are also most likely explained by surface effects.[12]

The upper limit of 10^{-19} cm^3 molecule^{-1} s^{-1} is 4 orders of magnitude smaller than the one previously reported in the literature,[2] and it makes reaction 1 unimportant in the stratosphere: the reaction of HCl with $ClONO_2$ becomes at least 4 or 5 orders of magnitude slower than reaction with OH.

Our experimental results do not rule out the occurrence of reaction 1 in the stratosphere as a heterogeneous process. However, given the relatively small collision rates with particulates $(10^{-4}–10^{-5}$ s$^{-1})^5$ and considering that both reactants have to be on the surface, we feel that it is not likely for such a heterogeneous process to contribute significantly to the release of Cl from HCl.

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A Magnetic Circular Dichroism Study of the 3p Rydberg States of Acetone

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The magnetic circular dichroism spectrum of acetone in the energy region of the 3p Rydberg states shows opposite sign B terms. It indicates that two excited states are contributing to the absorption in the region. The states are assigned as the two allowed 3p Rydbergs $^1A_1$ and $^1B_2$. It is shown, based on a previous ab-initio calculation and a simple B term calculation, that $^1B_2$ is the lower energy state.

In a recent electron impact study of the Rydberg states of acetone, Doering and McDiarmid[1] provided a new assignment of the Rydberg transitions in the 7.3–8.1-eV energy region. The high resolution obtained in their instrument enabled them to resolve

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and characterize almost all the bands previously observed in the optical absorption spectrum and at the same energies. According to their interpretation, only the forbidden 3p ($^1A_2$) Rydberg state is observed while the two allowed 3p components ($^1A_1$ and $^1B_2$ states) do not show up in the electron impact or optical spectra. Thus, they assign the energy loss spectrum to a forbidden 3p state