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proposed in situ measurement technique. NO$_3^-$(ClONO$_2$) does react with HNO$_3$ and
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Ion chemistry of $ClONO_2$ involving NO_3^- core ions: A detection scheme for $ClONO_2$ in the atmosphere

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Abstract. Rate constants and product branching ratios for reactions involving atmospherically interesting ions and $ClONO_2$ have been measured. H_3O^+ reacts rapidly with $ClONO_2$, but hydrates of H_3O^+ do not. This implies that $ClONO_2$ does not play a central role in the positive ion chemistry of the atmosphere. CO_3^- reacts with $ClONO_2$ to form NO_3^-. Both NO_3^- and $NO_3^-(H_2O)$ react with $ClONO_2$ to form $NO_3^-(ClONO_2)$. H_2O does not react with $NO_3^-(ClONO_2)$, which is essential to the proposed in situ measurement technique. $NO_3^-(ClONO_2)$ does react with HNO_3 and HCl, producing $NO_3^-(HNO_3)$ in both cases. The reaction of $NO_3^-(HCl)$ with $ClONO_2$ also produces $NO_3^-(HNO_3)$. These latter two efficient reactions, which are discussed in detail in a separate publication, are analogous to the efficient neutral heterogeneous reaction of HCl with $ClONO_2$ which is important in the chemistry of the Antarctic stratosphere. A detection scheme is presented for atmospheric $ClONO_2$ based on the reactions studied and utilizing mass spectrometry. A $ClONO_2$ detection limit of 10^7 molecules cm^{-3} is estimated based on the operating characteristics of current ion-molecule based mass spectrometric field instruments.

Introduction

The details of the chemical cycling of inorganic chlorine species and nitrogen oxide species (NO_y) in the stratosphere are critical to our understanding of stratospheric ozone chemistry. In the presence of polar stratospheric clouds (PSCs), the heterogeneous reactions of the chlorine reservoir species $ClONO_2$, HCl, and HOCl chemically transform these long-lived species into photoactive species which can lead to rapid and catalytic destruction of ozone. In the midlatitude stratosphere and in the absence of PSCs, the combination of photochemical life cycles of these species results in a relatively stable ozone concentration. The chemical life cycle of chlorine nitrate is especially important to the chemistry of the stratosphere because it is a member of both the inorganic chlorine and NO_y families. As such, chlorine nitrate couples these two important chemical families. Understanding the complex chemistry and changing concentration of chlorine nitrate is critical to a complete understanding of the chemistry of the atmosphere.

Despite the importance of chlorine nitrate to the chemistry of the stratosphere, few in situ measurements of its concentration in the atmosphere have been made [*Rinsland et al.*, 1985; *Raper et al.*, 1987; *Toon et al.*, 1993]. Current measurements include column abundance determinations, where a vertical profile is estimated from the spectral line shape [*Toon et al.*, 1993]. Detailed models of stratospheric chemistry, however, do not generally use these values of $ClONO_2$ but rather deduce the concentration of $ClONO_2$ from measurements of related species [*Salawitch et al.*, 1993]. Many

models assume that total inorganic chlorine is essentially divided between HCl and $ClONO_2$ (in the absence of PSCs) and therefore calculate the concentration of $ClONO_2$ from the difference between the total inorganic chlorine concentration, derived from N_2O measurements, and the measured HCl concentration [*Salawitch et al.*, 1993; *Webster et al.*, 1993]. Recently, *Webster et al.* [1993] made the first in situ spectroscopic determinations of the HCl concentration in the stratosphere. Their values, measured outside of the polar vortices, differ from previous determinations by as much as a factor of 2 [*Raper et al.*, 1987; *Webster et al.*, 1993]. If total inorganic chlorine is partitioned between HCl and $ClONO_2$, their measurements indicate that there is a corresponding error in the accepted $ClONO_2$ values [*Rodriguez*, 1993; *Webster et al.*, 1993]. The discrepancies between these different determinations represent significant differences in our overall understanding of the chemistry of the stratosphere. A direct in situ measurement of the concentration of $ClONO_2$ in the stratosphere would contribute significantly to a resolution of these discrepancies.

In situ ion composition measurements have proven to be a valuable tool in determining atmospheric concentrations of trace neutral species when combined with the knowledge of the chemistry and rate constants involved. Determination of concentrations of naturally abundant atmospheric species using ion chemistry has been developed mainly by the research groups of Arnold and Eisele, and their work has recently been reviewed by *Viggiano* [1993]. Detection of neutral species can be achieved by measurements of ambient atmospheric ions or, in a more elaborate apparatus, by measurements of product ions formed from reaction with ions produced in an active ion source. These mass spectrometric techniques combine the selectivity of ion-molecule

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chemistry with the sensitivity of mass spectrometry to yield a very powerful detection technique for neutral species abundant in only trace amounts. Measurements of a number of species in the parts per quadrillion range have been made. Negative ion composition measurements have been very successful in determining the concentrations of NO$_x$ and HNO$_x$ species [Arnold et al., 1992; Viggiano, 1993]. However, no detection scheme has been successfully devised previously for ClONO$_2$. In this paper we report kinetics measurements involving NO$_3^-$ core ions and ClONO$_2$, the latter species as both a ligand and a neutral reactant. We believe these data will make in situ determinations of the atmospheric ClONO$_2$ concentration possible using currently available mass spectrometric ion detection field instruments.

Experiment

The measurements were made using the Phillips Laboratory variable temperature-selected ion flow drift tube apparatus [Viggiano et al., 1990]. Instruments of this type have been the subject of review [Smith and Adams, 1988], and only those aspects important to the present study will be discussed in detail. Ions were created by electron impact in a high-pressure ion source (~0.1–1 torr). The ions were extracted from the source, mass selected in a quadrupole mass filter, and injected into a flow tube. Buffer gas was added through a Venturi inlet surrounding the ion injection orifice and transported the ions along the length of the flow tube. The Venturi inlet aids in injecting the ions at low energy, critical to the present experiments. Downstream, after the ions have had sufficient collisions with the buffer to thermalize, the neutral reactant is added. At the end of the flow tube, a small fraction of the ions are sampled through a 0.2-mm hole in a nose cone. The ions sampled are mass analyzed in a second quadrupole mass spectrometer and detected by a channel electron multiplier. Flow rates of the buffer and of the reactant gas were controlled and measured by MKS flow controllers. The entire flow tube could be heated or cooled. As will be explained below, cooling was necessary to perform some of the experiments presented. Rate constants were determined from the decay of the primary ion signal as a function of added neutral flow.

The weakly bonded cluster ions used in the present experiments required mild conditions to minimize both collisional breakup upon injection and thermal dissociation in the flow tube. NO$_3^-$ and NO$_3^-$(HNO$_3$) were made from NO$_2$ and a several percent HNO$_3$ impurity in our NO$_2$ sample. NO$_3^-$(HNO$_3$) is a strongly bonded cluster ion, and no special conditions were needed for working with it except low-injection energy. In contrast, it was quite difficult to form, inject, and detect a sufficient concentration of NO$_3^-$(H$_2$O). This ion was made from a mixture of NO$_2$ and H$_2$O. Our problems were traced to three sources: (1) instability of the ion in the ion source, (2) breakup of the ion upon injection and (3) thermal dissociation in the flow tube. First attempts at injecting NO$_3^-$(H$_2$O) into a He buffer at room temperature proved unsuccessful. We observed mainly NO$_3^-$ ion signal and a small mass 80 signal which we later identified as SO$_3^-$ (formed from impurities in the source from previous experiments) and not NO$_3^-$(H$_2$O). In order to make a sufficient quantity of NO$_3^-$(H$_2$O) we needed both to cool the system and to use a H$_2$ buffer. The cooling was necessary to prevent thermal dissociation in the buffer gas, which is a problem at

room temperature. This is based on the knowledge of the known association rate constant [Ikezoe et al., 1987] and thermodynamics [Keesee and Castleman, Jr., 1986] through $K = k_f/k_r$. The use of a H$_2$ buffer lowers the center of mass energy upon injection for the same laboratory frame energy [Viggiano, 1984]. Even with these steps, about equal parts of NO$_3^-$ and NO$_3^-$(H$_2$O) were initially present in the flow tube. The presence of both these ions does not affect our rate constant measurements. Both of these ions produce only NO$_3^-$(ClONO$_2$), and therefore product determination also was unaffected. NO$_3^-$(ClONO$_2$) was made by adding NO$_2$ and ClONO$_2$ to the source. Creation, injection, and detection of NO$_3^-$(ClONO$_2$) was easier than NO$_3^-$(H$_2$O) but more difficult than NO$_3^-$(HNO$_3$), reflecting the intermediate cluster bond strength of NO$_3^-$(ClONO$_2$). H$_3$O$^+$(H$_2$O)$_n$ ions were made from H$_2$O, and CO$_3^-$ was formed from CO$_2$.

The ClONO$_2$ was synthesized from ClF and HNO$_3$ by the method of Shack [1967] with some modification [Lloyd, 1993] and stored at 200 K. During the experiments, the ClONO$_2$ was heated to 233 K, and the vapor was added to the flow tube through a mass flow controller. At this temperature, little of the HNO$_3$ impurity present in the sample should be volatile. The flow rate of ClONO$_2$ was calibrated by using the heat capacity given by Miller et al. [1967]. In initial experiments the ClONO$_2$ sample was found to contain a large amount of HNO$_3$. After flowing the ClONO$_2$ for a time period of the order of an hour or two, the HNO$_3$ impurity was greatly reduced, presumably through conditioning of the inlet lines; that is, water on the inlet line surfaces had reacted away. The experiments required the use of a large amount of ClONO$_2$ which limited the number of reactions studied to date because of limited sample quantity, and further studies are planned. We estimate the uncertainty in our rate constants to be ±30% and the relative error to be 20%, slightly higher than our usual error limits.

Results

Table 1 lists the reactions studied and the temperatures at which the rate constants were measured. As explained in the experimental section, different ions were best studied at different temperatures. The limited amount of ClONO$_2$ sample we could obtain prevented us from making extensive temperature dependence measurements. Temperature dependence studies are planned for the future.

The group of reactions listed in Table 1 was chosen for the potential importance in the atmosphere both in terms of the chemistry of ambient ions and for detection of ClONO$_2$. The series H$_3$O$^+$(H$_2$O)$_n$ can be considered the starting point for much of the positive ion chemistry of the lower atmosphere, with the n = 3 or higher species being by far the predominant ions [Ferguson and Arnold, 1981]. The present results show that ClONO$_2$ does not react with H$_3$O$^+$(H$_2$O)$_{\geq 2}$. Essentially, all other positive ions in the lower atmosphere are more stable than H$_3$O$^+$(H$_2$O)$_n$ and will presumably also be unreactive toward ClONO$_2$. Therefore the positive ion chemistry of the atmosphere is essentially unaffected by the presence of ClONO$_2$.

The most important ambient negative ions are the series NO$_3^-$(HNO$_3$)$_n$ with n = 1 to 3 being the most abundant [Viggiano and Arnold, 1983]. Above 30 km, the series HSO$_4^-$(H$_2$SO$_4$)$_m$(HNO$_3$)$_n$ also becomes important. The present results show that NO$_3^-$(HNO$_3$) does not react ap-

Table 1. Rate Constants for Reactions Involving ClONO$_2$

Reaction	Rate Constant, cm^3 s^{-1}	Temperature, K
(1) NO$_3^-$ + ClONO$_2$ + H$_2$ → NO$_3^-$(ClONO$_2$) + H$_2$	3.0 (−10)[a]	232
(2) CO$_3^-$ + ClONO$_2$ → NO$_3^-$ + ClO + CO$_2$	2.1 (−9)	232
(3) NO$_3^-$(HNO$_3$) + ClONO$_2$ → products[b]	<2 (−11)[b]	232
(4) NO$_3^-$(H$_2$O) + ClONO$_2$ → NO$_3^-$(ClONO$_2$) + H$_2$O	1.8 (−9)	232
(5) NO$_3^-$(ClONO$_2$) + H$_2$O → products	n.r.[c]	283
(6) NO$_3^-$(ClONO$_2$) + HNO$_3$ → NO$_3^-$(HNO$_3$) + ClONO$_2$	1.1 (−9)	283
(7) NO$_3^-$(ClONO$_2$) + HCl → NO$_3^-$(HNO$_3$) + Cl$_2$ (94%) → NO$_3^-$(HCl) + ClONO$_2$ (6%)	1.5 (−9)	283
(8) NO$_3^-$(HCl) + ClONO$_2$ → NO$_3^-$(HNO$_3$) + Cl$_2$ (98%)[d] → NO$_3^-$(ClONO$_2$) + HCl (2%)	1.8 (−9)	233
(9) H$_3$O$^+$ + ClONO$_2$ → H$^+$ · ClONO$_2$ + H$_2$O (31%)[e] → NO$_2^+$ + H$_2$OHOCl (6%)[e,f] → NO$_2^+$(H$_2$O) + HOCl (63%)[e]	2.9 (−9)	233
(10) H$_3$O$^+$(H$_2$O) + ClONO$_2$ → products[g]	<1.3 (−10)[g]	233
(11) H$_3$O$^+$(H$_2$O)$_2$ + ClONO$_2$ → products	n.r.[c]	233
(12) H$_3$O$^+$(H$_2$O)$_3$ + ClONO$_2$ → products	n.r.[c]	233

[a] 3.0 (−10) means 3 × 10^{-10}.

[b] No product observed.

[c] No reaction, no decline in reactant ion signal.

[d] Estimated effect of HNO$_3$ impurity is less than 1 percentage point.

[e] Branching ratio not corrected for HNO$_3$ impurity, correction will increase H$^+$ · ClONO$_2$ with respect to the other products.

[f] Neutral product is written as a dimer since monomer formation is endothermic by 0.4 eV. Dimer bond strength is unknown but formation should make the reaction close to thermoneutral.

[g] HNO$_3$ impurity could account for the reactivity.

preciably with ClONO$_2$, and it is therefore expected that the higher clusters are unreactive as well. The more stable ions HSO$_4^-$(H$_2$SO$_4$)$_m$(HNO$_3$)$_n$ also are not expected to react.

CO$_3^-$ and CO$_3^-$(H$_2$O) have been used successfully to monitor the concentrations of NO, NO$_2$, HNO$_2$, and HNO$_3$ [Arnold et al., 1992]. Here we find that CO$_3^-$ reacts rapidly with ClONO$_2$ to form NO$_3^-$. However, this is not a useful reaction for detecting the presence of ClONO$_2$ since NO, NO$_2$, N$_2$O$_5$, and HNO$_3$ also form NO$_3^-$ from reaction with CO$_3^-$ [Ikezoe et al., 1987]. In fact, the reaction of ClONO$_2$ with CO$_3^-$ may obscure or complicate the detection of some of these other species when ClONO$_2$ concentrations are comparable to that of the nitrogen oxide species of interest.

Another series of ions that is easy to create in active ion source measurements is NO$_3^-$ and its hydrates, NO$_3^-$(H$_2$O)$_n$, particularly the first hydrate (where $n = 1$). The present results show that both NO$_3^-$ and NO$_3^-$(H$_2$O) react with ClONO$_2$ to form NO$_3^-$(ClONO$_2$). These reactions each form an ion, which can be uniquely connected with the presence of ClONO$_2$, an important condition for the accurate determination of atmospheric concentrations. The clustering rate between NO$_3^-$ and ClONO$_2$ is relatively slow and would appear to reduce the sensitivity of using this reaction as a ClONO$_2$ detector. One must note, however, that our results refer to a pressure of only 0.2 torr, while the region of interest for atmospheric detection of ClONO$_2$, 10-25 km, has a pressure of ~20 − 200 torr. One expects that this reaction will saturate under atmospheric conditions and cluster at approximately the collision rate, that is, the rate constant will be the same as that for NO$_3^-$(H$_2$O). Direct measurements of this rate constant in a high-pressure apparatus

are needed to verify this assumption. In summary, NO$_3^-$(ClONO$_2$) should be formed very rapidly by both NO$_3^-$ and NO$_3^-$(H$_2$O) under atmospheric conditions.

While this scheme includes a rapid means of forming an ion species that can be attributed unambiguously to ClONO$_2$, there are potentially interfering reactions. Fortunately, H$_2$O does not react with NO$_3^-$(ClONO$_2$). If this reaction were to proceed, the large abundance of H$_2$O in the atmosphere would ensure that NO$_3^-$(ClONO$_2$) would be lost before it could be detected. There are nevertheless several reactions that could interfere with this detection scheme. HNO$_3$ switches ClONO$_2$ out of NO$_3^-$(ClONO$_2$) rapidly to form NO$_3^-$(HNO$_3$). HCl reacts with NO$_3^-$(ClONO$_2$) to form NO$_3^-$(HNO$_3$). This last reaction and the reaction of NO$_3^-$(HCl) with ClONO$_2$ are analogous to the neutral heterogeneous reaction of ClONO$_2$ with HCl which is important in the mechanism of stratospheric ozone loss in the polar winter. These reactions are discussed in detail in a separate publication [Van Doren et al., 1994].

The ion chemical detection scheme derived from our measurements for determining the concentration of ambient ClONO$_2$ is as follows. A chemical ionization source is set up to produce NO$_3^-$ and NO$_3^-$(H$_2$O) as the primary ions. These ions are injected into a flow reactor connected to a mass spectrometer. In the flow tube, reactions (1) and (4) both produce NO$_3^-$(ClONO$_2$). The rate constants for both of these reactions are expected to be large at stratospheric temperatures and pressures and for the present purposes can be assumed to be equal to the rate constant for reaction (4). Total depletion of the NO$_3^-$ and NO$_3^-$(H$_2$O) primary ions must be kept small, that is, less than 10%. This ensures that

no appreciable secondary reaction of $NO_3^-(ClONO_2)$ will occur; that is, the derived concentration will not be affected by secondary reactions by more than 10%. For low total depletion of primary ions, the concentration of $ClONO_2$ is given as

$$[ClONO_2] = \frac{[NO_3^-(ClONO_2)]}{([NO_3^-]+[NO_3^-(H_2O)])*1.8(-9)*t} , \quad (13)$$

where t is the reaction time in the flow tube and the $ClONO_2$ concentration is in the units of molecule cm^{-3}. It should be noted that only relative ion signals need to be measured.

The concentration detection limit of this scheme can be estimated as follows: The minimum ion ratio that can be detected in mass spectrometers of the type used for in situ atmospheric ion detection by the Arnold and Eisele groups is on the order of 10^{-4}. Typical reaction times in these instruments are 10 ms [*Viggiano*, 1993]. These parameters yield a detection limit of 10^7 molecules cm^{-3}. This estimate has been confirmed by F. Arnold (private communication, 1993) currently the only active researcher flying the type of instrument needed for these measurements. Estimated $ClONO_2$ concentrations in the atmosphere are in the part per billion range, or 4×10^9 molecules cm^{-3} at 15 km. The minimum detection limit of the detection scheme presented greatly exceeds that needed to make measurements of typical concentrations of atmospheric $ClONO_2$ and indicates that accurate measurements can be made under conditions where the $ClONO_2$ concentration is extremely small. When ClO concentrations are comparable to or greater than $ClONO_2$ concentrations, it may also be possible to detect ClO by this technique by titrating the ClO with NO_2.

In addition to the direct determination of atmospheric $ClONO_2$ concentrations, this method is likely to provide simultaneous determinations of the concentrations of other important species such as HCl, HOCl, HNO_3, HNO_2, and H_2SO_4. Such determinations are possible because most acids cluster to NO_3^- and switch H_2O out of $NO_3^-(H_2O)$ [*Ikezoe et al.*, 1987]. The acids HNO_3, HCl, and HNO_2 have been measured by this or similar techniques previously [*Viggiano*, 1993]. For several of these species the rate constants needed are not known, and future work will focus on measuring the pertinent rate coefficients. The most accurate measurements would involve in-flight calibration using controlled releases of the compounds of interest into the flow tube. Such calibrations are currently possible.

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