Abstract. Rate constants and product branching ratios for reactions involving atmospherically interesting ions and CIONO₂ have been measured. H₂O⁺ reacts rapidly with CIONO₂, but hydrates of H₂O⁺ do not. This implies that CIONO₂ does not play a central role in the positive ion chemistry of the atmosphere. CO₂ reacts with CIONO₂ to form NO₃⁻. Both NO₃⁻ and NO₂⁻(H₂O) react with CIONO₂ to form NO₂⁻(CIONO₂). H₂O does not react with NO₂⁻(CIONO₂), which is essential to the proposed in situ measurement technique. NO₃⁻(CIONO₂) does react with HNO₃ and HCl, producing NO₂⁻(HNO₃) in both cases. The reaction of NO₂⁻(HCl) with CIONO₂ also produces NO₃⁻(HNO₃). 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 CIONO₂ which is important in the chemistry of the Antarctic stratosphere. A detection scheme is presented for atmospheric CIONO₂ based on the reactions studied and utilizing mass spectrometry. A CIONO₂ detection limit of 10⁷ molecules cm⁻³ is estimated based on the operating characteristics of current ion-molecule based mass spectrometric field instruments.
Ion chemistry of $\text{CINO}_2$ involving $\text{NO}_3^-$ core ions: A detection scheme for $\text{CINO}_2$ in the atmosphere

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Abstract. Rate constants and product branching ratios for reactions involving atmospherically interesting ions and $\text{CINO}_2$ have been measured. $\text{H}_3\text{O}^+$ reacts rapidly with $\text{CINO}_2$, but hydrates of $\text{H}_3\text{O}^+$ do not. This implies that $\text{CINO}_2$ does not play a central role in the positive ion chemistry of the atmosphere. $\text{CO}_2^-$ reacts with $\text{CINO}_2$ to form $\text{NO}_3^-$. Both $\text{NO}_3^-$ and $\text{NO}_3^-\text{(H}_2\text{O)}$ react with $\text{CINO}_2$ to form $\text{NO}_2^-\text{(CINO}_2\text{)}$. $\text{H}_2\text{O}$ does not react with $\text{NO}_3^-\text{(CINO}_2\text{)}$, which is essential to the proposed in situ measurement technique. $\text{NO}_2^-\text{(CINO}_2\text{)}$ does react with $\text{HNO}_3$ and $\text{HCl}$, producing $\text{NO}_3^-\text{(HNO}_3\text{)}$ in both cases. The reaction of $\text{NO}_3^-\text{(HCl)}$ with $\text{CINO}_2$ also produces $\text{NO}_3^-\text{(HNO}_3\text{)}$. These latter two efficient reactions, which are discussed in detail in a separate publication, are analogous to the efficient neutral heterogeneous reaction of $\text{HCl}$ with $\text{CINO}_2$ which is important in the chemistry of the Antarctic stratosphere. A detection scheme is presented for atmospheric $\text{CINO}_2$, based on the reactions studied and utilizing mass spectrometry. A $\text{CINO}_2$ 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 ($\text{NO}_x$) 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 $\text{CINO}_2$, $\text{HCl}$, and $\text{HOCI}$ 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 $\text{NO}_x$ 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 $\text{CINO}_2$ but rather deduce the concentration of $\text{CINO}_2$ from measurements of related species [Salawitch et al., 1993; Rodriguez, 1993]. Many models assume that total inorganic chlorine is essentially divided between $\text{HCl}$ and $\text{CINO}_2$ (in the absence of PSCs) and therefore calculate the concentration of $\text{CINO}_2$ from the difference between the total inorganic chlorine concentration, derived from $\text{N}_2\text{O}$ measurements, and the measured $\text{HCl}$ concentration [Salawitch et al., 1993; Webster et al., 1993]. Recently, Webster et al. [1993] made the first in situ spectroscopic determinations of the $\text{HCl}$ 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 $\text{HCl}$ and $\text{CINO}_2$, their measurements indicate that there is a corresponding error in the accepted $\text{CINO}_2$ 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 $\text{CINO}_2$ 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
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 \( \text{NO}_3 \) and \( \text{HNO}_2 \) species [Arnold et al., 1992; Viggiano, 1993]. However, no detection scheme has been successfully devised previously for \( \text{CINO}_2 \). In this paper we report kinetics measurements involving \( \text{NO}_3^- \) core ions and \( \text{CINO}_2 \), the latter species as both a ligand and a neutral reactant. We believe these data will make in situ determinations of the atmospheric \( \text{CINO}_2 \) 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. \( \text{NO}_3^- \) and \( \text{NO}_5^- \) (\( \text{HNO}_3 \)) were made from \( \text{NO}_2 \) and a several percent \( \text{HNO}_3 \) impurity in our \( \text{NO}_2 \) sample. \( \text{NO}_2^- \) (\( \text{HNO}_2 \)) 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 \( \text{NO}_5^- \) (\( \text{H}_2 \text{O} \)). This ion was made from a mixture of \( \text{NO}_2 \) and \( \text{H}_2 \text{O} \). 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 \( \text{NO}_5^- \) (\( \text{H}_2 \text{O} \)) into a He buffer at room temperature proved unsuccessful. We observed mainly \( \text{NO}_3^- \) ion signal and a small mass 80 signal which we later identified as \( \text{SO}_4^- \) (formed from impurities in the source from previous experiments) and not \( \text{NO}_5^- \) (\( \text{H}_2 \text{O} \)). In order to make a sufficient quantity of \( \text{NO}_5^- \) (\( \text{H}_2 \text{O} \)) we needed both to cool the system and to use a \( \text{H}_2 \) 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 [Keezee and Castleman, Jr., 1986] through \( K = k/k_s \). The use of a \( \text{H}_2 \) 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 \( \text{NO}_3^- \) and \( \text{NO}_5^- \) (\( \text{H}_2 \text{O} \)) 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 \( \text{NO}_3^- \) (\( \text{CINO}_2 \)), and therefore product determination also was unaffected. \( \text{NO}_3^- \) (\( \text{CINO}_2 \)) was made by adding \( \text{NO}_2 \) and \( \text{CINO}_2 \) to the source. Creation, injection, and detection of \( \text{NO}_5^- \) (\( \text{CINO}_2 \)) was easier than \( \text{NO}_3^- \) (\( \text{H}_2 \text{O} \)) but more difficult than \( \text{NO}_3^- \) (\( \text{HNO}_3 \)), reflecting the intermediate cluster bond strength of \( \text{NO}_5^- \) (\( \text{CINO}_2 \)). \( \text{H}_2 \text{O}^- \) (\( \text{H}_2 \text{O} \)) ions were made from \( \text{H}_2 \text{O} \), and \( \text{CO}_2^- \) was formed from \( \text{CO}_2 \).

The \( \text{CINO}_2 \) was synthesized from \( \text{CIF} \) and \( \text{HNO}_3 \) by the method of Shack [1967] with some modification [Lloyd, 1993] and stored at 200 K. During the experiments, the \( \text{CINO}_2 \) 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 \( \text{HNO}_3 \) impurity present in the sample should be volatile. The flow rate of \( \text{CINO}_2 \) was calibrated by using the heat capacity given by Miller et al. [1967]. In initial experiments the \( \text{CINO}_2 \) sample was found to contain a large amount of \( \text{HNO}_3 \). After flowing the \( \text{CINO}_2 \) for a time period of the order of an hour or two, the \( \text{HNO}_3 \) 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 \( \text{CINO}_2 \) 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 \( \text{CINO}_2 \) 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 \( \text{CINO}_2 \). The series \( \text{H}_2 \text{O}^- \) (\( \text{H}_2 \text{O} \)) 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 \( \text{CINO}_2 \) does not react with \( \text{H}_2 \text{O}^- \) (\( \text{H}_2 \text{O} \)). Essentially, all other positive ions in the lower atmosphere are more stable than \( \text{H}_2 \text{O}^- \) (\( \text{H}_2 \text{O} \)), and will presumably also be unreactive toward \( \text{CINO}_2 \). Therefore the positive ion chemistry of the atmosphere is essentially unaffected by the presence of \( \text{CINO}_2 \).

The most important ambient negative ions are the series \( \text{NO}_3^- \) (\( \text{HNO}_3 \)), with \( n = 1 \) to 3 being the most abundant [Viggiano and Arnold, 1983]. Above 30 km, the series \( \text{HSO}_4^- \) (\( \text{H}_2 \text{SO}_4 \)) (\( \text{HNO}_3 \)) also becomes important. The present results show that \( \text{NO}_3^- \) (\( \text{HNO}_3 \)) does not react ap-
precisely with ClONO₂, and it is therefore expected that the higher clusters are unreactive as well. The more stable ions HSO₃⁻(H₂SO₄)ₙ(HNO₃)ₙ also are not expected to react.

CO₃⁻ and CO₃(H₂O) have been used successfully to monitor the concentrations of NO, NO₂, HNO₃, and HNO₃ [Arnold et al., 1992]. Here we find that CO₃⁻ reacts rapidly with ClONO₂ to form NO₃⁻. However, this is not a useful reaction for detecting the presence of ClONO₂ since NO, NO₂, N₂O₅, and HNO₃ also form NO₃⁻ from reaction with CO₃⁻ [Jeeze et al., 1987]. In fact, the reaction of ClONO₂ with CO₃⁻ may obscure or complicate the detection of some of these other species when ClONO₂ 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 NO₃⁻ and its hydrates, NO₃⁻(H₂O)ₙ, particularly the first hydrate (where n = 1). The present results show that both NO₃⁻ and NO₃⁻(H₂O) react with ClONO₂ to form NO₃⁻(ClONO₂). These reactions each form an ion, which can be uniquely connected with the presence of ClONO₂, an important condition for the accurate determination of atmospheric concentrations. The clustering rate between NO₃⁻ and ClONO₂ is relatively slow and would appear to reduce the sensitivity of using this reaction as a ClONO₂ 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 ClONO₂, 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 NO₃⁻(H₂O). Direct measurements of this rate constant in a high-pressure apparatus are needed to verify this assumption. In summary, NO₃⁻(ClONO₂) should be formed very rapidly by both NO₃⁻ and NO₃⁻(H₂O) under atmospheric conditions.

While this scheme includes a rapid means of forming an ion species that can be attributed unambiguously to ClONO₂, there are potentially interfering reactions. Fortunately, H₂O does not react with NO₃⁻(ClONO₂). If this reaction were to proceed, the large abundance of H₂O in the atmosphere would ensure that NO₃⁻(ClONO₂) would be lost before it could be detected. There are nevertheless several reactions that could interfere with this detection scheme. HNO₃ switches ClONO₂ out of NO₃⁻(ClONO₂) rapidly to form NO₃⁻(HNO₃). HCl reacts with NO₃⁻(ClONO₂) to form NO₃⁻(ClONO₂) + HCl(2%). 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.

### Table 1. Rate Constants for Reactions Involving ClONO₂

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant, Temperature, cm⁻³ s⁻¹</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) NO₃⁻ + ClONO₂ + H₂ → NO₃⁻(ClONO₂) + H₂</td>
<td>3.6 (-10)⁺</td>
<td>232</td>
</tr>
<tr>
<td>(2) CO₃⁻ + ClONO₂ → NO₃⁻ + Cl₂ + CO₂</td>
<td>2.1 (-9)</td>
<td>232</td>
</tr>
<tr>
<td>(3) NO₃⁻(HNO₃) + ClONO₂ → productsᵇ</td>
<td>&lt;2 (-11)ᵇ</td>
<td>232</td>
</tr>
<tr>
<td>(4) NO₃⁻(H₂O) + ClONO₂ → NO₃⁻(ClONO₂) + H₂O</td>
<td>1.8 (-9)</td>
<td>232</td>
</tr>
<tr>
<td>(5) NO₃⁻(ClONO₂) + H₂O → products</td>
<td>n.r.ᶜ</td>
<td>283</td>
</tr>
<tr>
<td>(6) NO₃⁻(ClONO₂) + HNO₃ → NO₃⁻(HNO₃) + ClONO₂</td>
<td>1.1 (-9)</td>
<td>283</td>
</tr>
<tr>
<td>(7) NO₃⁻(ClONO₂) + HCl → NO₃⁻(HCl) + ClONO₂(6%)</td>
<td>1.5 (-9)</td>
<td>283</td>
</tr>
<tr>
<td>(8) NO₃⁻(HCl) + ClONO₂ → NO₃⁻(HNO₃) + ClONO₂(98%)</td>
<td>1.8 (-9)</td>
<td>233</td>
</tr>
<tr>
<td>(9) H₂O⁺ + ClONO₂ → H⁺ + ClONO₂ + H₂O (31%)</td>
<td>2.9 (-9)</td>
<td>233</td>
</tr>
<tr>
<td>(10) H₂O⁺(H₂O) + ClONO₂ → products</td>
<td>&lt;1.3 (-10)ᵈ</td>
<td>233</td>
</tr>
<tr>
<td>(11) H₂O⁺(H₂O₂) + ClONO₂ → products</td>
<td>n.r.ᶜ</td>
<td>233</td>
</tr>
<tr>
<td>(12) H₂O⁺(H₂O₃) + ClONO₂ → products</td>
<td>n.r.ᶜ</td>
<td>233</td>
</tr>
</tbody>
</table>

⁺3.0 (-10) means 3 × 10⁻¹⁰.
ᵇNo product observed.
ᶜNo reaction, no decline in reactant ion signal.
ᵈEstimated effect of HNO₃ impurity is less than 1 percentage point.
ᵉBranching ratio not corrected for HNO₃ impurity, correction will increase H⁺ reaction for ClONO₂ with respect to the other products.
ᶠNeutral 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.
ᵍHNO₃ impurity could account for the reactivity.

In the flow tube, reactions (1) and (4) both produce NO₃⁻(ClONO₂). 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 NO₃⁻ and NO₃⁻(H₂O) primary ions must be kept small, that is, less than 10%. This ensures that
no appreciable secondary reaction of $\text{NO}_2^-(\text{CIONO}_2)$ 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 CIONO$_2$ is given as

$$[\text{CIONO}_2] = \frac{[\text{NO}_2^-\text{(CIONO}_2)]}{([\text{NO}_2^-]+[\text{NO}_2^-\text{(H}_2\text{O}_2)]) \times 1.8^{-9} t}, \quad (13)$$

where $t$ is the reaction time in the flow tube and the CIONO$_2$ 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 CIONO$_2$ concentrations in the atmosphere are in the part per billion range, or $4 \times 10^3$ 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 CIONO$_2$ and indicates that accurate measurements can be made under conditions where the CIONO$_2$ concentration is extremely small. When CIO concentrations are comparable to or greater than CIONO$_2$ concentrations, it may also be possible to detect CIO by this technique by titrating the CIO with NO$_2$.

In addition to the direct determination of atmospheric CIONO$_2$ 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$_2$SO$_4$. Such determinations are possible because most acids cluster to NO$_2^-$ and switch H$_2$O out of NO$_3^-(\text{H}_2\text{O})$ [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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