

# Rate Enhancement of the Reaction of HCl with ClONO<sub>2</sub> by Ions: Implications for the Mechanisms of Stratospherically Important Heterogeneous Reactions

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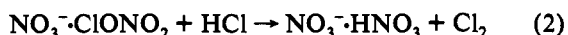
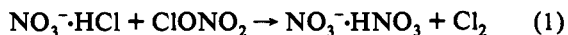
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We report the first observation of the ion-assisted neutral reaction of HCl with ClONO<sub>2</sub>. These two species react efficiently in the gas phase to form nitric acid and chlorine when one or the other is clustered to an NO<sub>3</sub><sup>-</sup> core ion:



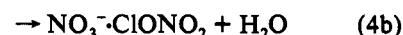
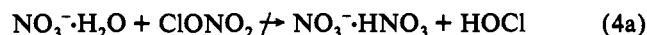
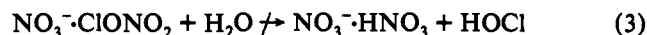
Utilizing a selected ion flow tube,<sup>1,2</sup> we find that reaction 1 proceeds with a rate coefficient of  $1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 233 K and that reaction 2 proceeds with a rate coefficient of  $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 283 K, values near the collision rate coefficient.<sup>3</sup> Minor ( $\leq 4\%$ ) channels involving ligand switching were also observed. In contrast, the rate coefficient for the neutral species HCl and ClONO<sub>2</sub> is small,<sup>4</sup>  $< 1 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ . Few reactions of this type, where the core ion enhances the rate of the reaction without apparently being chemically transformed, have been reported.<sup>5,6</sup> All previous studies have involved reactions of neutral species clustered to alkali positive ions. Reactions 1 and 2 are the fastest ion-assisted reactions studied to date and are the first instances where the effect of the reactants' organization, i.e., which neutral is initially clustered to the ion, could be probed.

Rate enhancement of the reaction of HCl with ClONO<sub>2</sub> also occurs on a variety of water-based surfaces.<sup>4,7-13</sup> In fact, the efficient heterogeneous reaction of HCl with ClONO<sub>2</sub> on polar stratospheric clouds plays an important role in the catalytic

destruction of polar stratospheric ozone.<sup>14</sup> We find that the efficiency of the ion-assisted reaction is similar to that of the heterogeneous reaction,  $\sim 50\%$  versus  $\sim 30\%$ , respectively.<sup>4</sup>

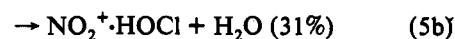
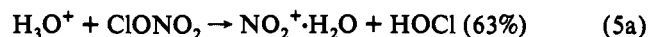
Also of importance in the chemistry of the polar stratosphere is the heterogeneous reaction of ClONO<sub>2</sub> with H<sub>2</sub>O to form HOCl + HNO<sub>3</sub>.<sup>4,7-13</sup> This reaction is inefficient in the gas phase<sup>4</sup> ( $k < 2 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$ ) but is very efficient in the presence of a variety of surfaces ( $\sim 1-100\%$ ).<sup>4,7-13</sup>

We investigated the reactions



In contrast to the reaction with HCl, the NO<sub>3</sub><sup>-</sup> ion-assisted neutral reaction of ClONO<sub>2</sub> with H<sub>2</sub>O to form HOCl + HNO<sub>3</sub> was found to be slow, i.e., the rate coefficients for both reactions 3 and 4a are  $< 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . Reaction 4a is exothermic ( $-39 \text{ kJ mol}^{-1}$ ).<sup>15</sup> The observations of reactions 2 and 4b place limits on the cluster bond energy of NO<sub>3</sub><sup>-</sup>·ClONO<sub>2</sub>:  $61 \text{ kJ mol}^{-1} \leq D(\text{NO}_3^- \cdot \text{ClONO}_2) \leq 172 \text{ kJ mol}^{-1}$ . These limits are not sufficient to determine whether reaction 3 is thermodynamically allowed. Ligand switching was observed in the reaction of NO<sub>3</sub><sup>-</sup>·H<sub>2</sub>O with ClONO<sub>2</sub> with a near collisional rate coefficient of  $1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 232 K.

While ClONO<sub>2</sub> and H<sub>2</sub>O were not observed to react when either of these neutrals was clustered to NO<sub>3</sub><sup>-</sup>, they appear to react when the "core" ion is H<sup>+</sup>, i.e., when the reactant ion is H<sub>3</sub>O<sup>+</sup>. Specifically, we observe the formation of protonated nitric acid,<sup>3</sup> known to have the structure NO<sub>2</sub><sup>+</sup>·H<sub>2</sub>O.<sup>16,17</sup>



NO<sub>2</sub><sup>+</sup>·HOCl and NO<sub>2</sub><sup>+</sup> are also formed. These products are consistent with the expected neutral reaction products (HOCl + HNO<sub>3</sub>), as discussed below. Reaction 5c is approximately thermoneutral; formation of separated HOCl and H<sub>2</sub>O neutrals would be 40 kJ/mol endothermic.<sup>15</sup> Unlike reactions 1 and 2, however, the reactant core ion is not maintained in reaction 5. We find the rate coefficient for reaction 5 to be  $2.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 233 K. Water clusters of H<sub>3</sub>O<sup>+</sup> react inefficiently if at all ( $k \leq 1.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 233 K for H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O) + ClONO<sub>2</sub>, where the observed reactivity may be due entirely or in part to an HNO<sub>3</sub> impurity in the ClONO<sub>2</sub>; no reaction was observed for H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O)<sub>2,3</sub> + ClONO<sub>2</sub>).

The ion NO<sub>2</sub><sup>+</sup>·HOCl arises from proton transfer (structure is given in ref 18) and indicates that the proton affinity of ClONO<sub>2</sub> is  $> 697 \text{ kJ mol}^{-1}$ . Calculations by Lee and Rice<sup>18</sup> yield a value of  $740 \pm 13 \text{ kJ mol}^{-1}$ , consistent with our results.

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(3) ClONO<sub>2</sub> sample was held at 233 K (where vapor pressure of HNO<sub>3</sub> impurity is negligible), and vapor was added to the flow tube. A minor HNO<sub>3</sub> impurity ( $\sim 10\%$ ) was present in the neutral flow due to reactions with trace water on inlet lines.

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Nelson and Okumura,<sup>19</sup> using a beam-collision cell apparatus, also observed the formation of  $\text{NO}_2^+$  and  $\text{NO}_2^+\cdot\text{H}_2\text{O}$  in the reaction of protonated water clusters with  $\text{ClONO}_2$ . Our results differ from theirs<sup>19</sup> in several ways: (1) they did not observe proton-transfer product ions, (2) they found  $\text{NO}_2^+$  as the primary product, and (3) they observed reaction between  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  ( $n \geq 2$ ) and  $\text{ClONO}_2$ . We attribute these differences to the higher collision energies ( $>0.5$  eV) in their experiment compared with our thermalized (233 K) reactants.

The first observations of the rate enhancement of neutral gas-phase reactions by association with ions were made at the NOAA laboratory in 1982 and 1983.<sup>5,20</sup> Viggiano et al.<sup>6</sup> pursued the origin of these enhancements, finding that the enhancement was in part due to a distortion of the neutral geometry toward the transition state in the presence of the ion. Such an explanation is consistent with the rate enhancement observed in the reactions reported here but does not relate the critical role the ion plays in the present situation.

We suggest that the "core" ions in reactions 1 and 2 are intimately involved in the reaction mechanism. Specifically, the ion-dipole bond energy gained upon initial association of the reactants allows an endothermic<sup>15</sup> proton transfer (37 kJ mol<sup>-1</sup> for isolated reactants) from HCl to  $\text{NO}_3^-$ . The  $\text{Cl}^-$  then attacks the chlorine in  $\text{ClONO}_2$  to form  $\text{Cl}_2$  and  $\text{NO}_3^-$ . This is supported by recent results from Okumura and co-workers, who found that the reaction of  $\text{Cl}^-$  with  $\text{ClONO}_2$  is efficient.<sup>21</sup> In the proposed mechanism, the nascent product ion will contain an  $\text{NO}_3^-$  core formed from  $\text{ClONO}_2$ , different from the  $\text{NO}_3^-$  core found in the reactants. Subsequent rapid proton transfer in the  $\text{NO}_3^- \cdot \text{HNO}_3$  product ion, however, will erase any such distinction. Facilitation of the neutral reaction of  $\text{ClONO}_2$  with HCl *via* initial proton transfer in the ion-dipole complex formed is also consistent with the lack of observation of reactions 3 and 4a, since proton transfer from  $\text{H}_2\text{O}$  to  $\text{NO}_3^-$  is very endothermic<sup>15</sup> ( $\sim 277$  kJ mol<sup>-1</sup> for the isolated reactants). This mechanism suggests that other ions

which can proton transfer with HCl within the ion-dipole complex will also facilitate the apparent neutral reaction, e.g., the reaction of  $\text{Br}^- \cdot \text{HCl}$  with  $\text{ClONO}_2$ .

The ionic reaction mechanism operative in reactions 1 and 2 may form the basis of the mechanism involved in the neutral heterogeneous reactions occurring in the atmosphere. Specifically, proton transfer from HCl to water will allow  $\text{Cl}^-$  to react with  $\text{ClONO}_2$ . Indeed, experimental evidence has led many researchers to suggest that the heterogeneous neutral reactions of  $\text{HCl} + \text{ClONO}_2$  and of  $\text{H}_2\text{O} + \text{ClONO}_2$  proceed through ionic reaction mechanisms.<sup>8-11,13,21-24</sup>

The gas-phase ion-molecule reaction between  $\text{H}_3\text{O}^+$  and  $\text{ClONO}_2$  is also likely to proceed *via* an initial proton transfer, forming the  $\text{NO}_2^+ \cdot \text{HOCl}$  ion. This product is observed in about one-third of the reactive collisions. Calculations by Lee and Rice<sup>18</sup> indicate that  $\text{NO}_2^+ \cdot \text{H}_2\text{O}$  is more strongly bound than  $\text{NO}_2^+ \cdot \text{HOCl}$ . Therefore, in about two-thirds of the reactive collisions,  $\text{H}_2\text{O}$  replaces HOCl before the products separate, yielding the observed product ion  $\text{NO}_2^+ \cdot \text{H}_2\text{O}$ . Finally, in a small fraction of the reactive encounters, the bare ion  $\text{NO}_2^+$  exits the reactive complex. Nelson and Okumura's observations support this hypothesis.<sup>19</sup>

Again, we suggest that the ion-molecule reaction mechanism for reaction 5 may form the basis of the mechanism for the reaction of  $\text{H}_2\text{O}$  with  $\text{ClONO}_2$  occurring on surfaces in the atmosphere. Specifically, proton transfer from  $\text{H}_3\text{O}^+$  present in the acidic stratospheric aerosols to adsorbed  $\text{ClONO}_2$  may initiate the chemical transformation. This has also been suggested by Okumura and co-workers.<sup>19</sup> Finally, since recent reports suggest that under most conditions the apparent reaction of HCl with  $\text{ClONO}_2$  on surfaces begins with the reaction of  $\text{ClONO}_2$  with available  $\text{H}_2\text{O}$ ,<sup>8-11,13</sup> the ionic mechanism in the reaction of  $\text{H}_3\text{O}^+ + \text{ClONO}_2$  may also be important in the atmospheric reaction of HCl with  $\text{ClONO}_2$ .

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