Gas Phase Reactions of Cl_2O with $NO^-_{x=2,3}\cdot(D_2O)_{n=0-2}$ and $Cl^-\cdot(D_2O)_{n=0-2}$[†]

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The results of laboratory measurements are reported for the reactions of Cl_2O with $NO_2^-\cdot(D_2O)_{n=0-2}$, $NO_3^-\cdot(D_2O)_{n=0-2}$, and $Cl^-\cdot(D_2O)_{n=0-2}$. These were studied using a flow-tube apparatus at several temperatures within the range 168−298 K and at a helium buffer gas pressure of 0.30 ± 0.02 Torr. Rate constants for primary reactions and product ions observed in various reaction sequences are reported, along with a discussion of possible reaction mechanisms. The findings contribute to a further mechanistic understanding of ionic reactions as well as other heterogeneous ones involving chlorine-containing molecules. Interestingly, evidence for a water-catalyzed reaction between Cl_2O and Cl^-/NO_3^- was obtained. Also, the present findings suggest that several ionic reactions may lead to the formation of $ClONO_2$ as a neutral product. Finally, limits on the electron affinity of Cl_2O are determined to be $2.52\ \text{eV} \leq \text{EA}(Cl_2O) \leq 3.617\ \text{eV}$.

Introduction

Heterogeneous reactions of chlorine compounds on polar stratospheric clouds (PSCs) are now recognized[1] to play an important role in the ozone depletion in the Antarctic and Arctic. On these particles, relatively inert chlorine reservoir species, $ClONO_2$ and HCl, are converted to photolizable forms, Cl_2 and HOCl. However, the composition of the PSCs and their formation, growth, and chemical reactivity are not fully elucidated.[2] Several researchers have suggested that ionic mechanisms may be involved in heterogeneous reactions occurring on PSC surfaces.[3] Recent laboratory studies[4] on the $ClONO_2$/water and N_2O_5/water systems show that ionization and solvation are fundamental features of a heterogeneous mechanism by which chlorine can be reactivated by PSCs.

In the present work we report the results on the reactions of dichloride monoxide, Cl_2O, with the anions $NO^-_{x=2,3}\cdot(D_2O)_{n=0-2}$ and $Cl^-\cdot(D_2O)_{n=0-2}$. The atmospheric concentration of Cl_2O is very low[5] (10^{-17}), and this species is not normally included in present atmospheric models. However, a study of its reactivity may be useful for a better understanding of the atmospheric chemistry of other chlorine-containing species (e.g. ClO, ClOOCl) which are currently thought to play an important role in the destruction of ozone in the polar stratosphere. Also, laboratory studies of the reactivity of bare ions and their clusters provide the key for a better fundamental understanding of the processes that occur on the surfaces or within aerosols and cloud particles and may help to elucidate the mechanisms of catalytic activity of heterogeneous reactions. The attachment of solvent molecules to the ion may modify both the potential energy surface and collision dynamics and can have a profound influence on the mechanisms and reactivity of ions. Finally, Cl_2O is commonly used as a reagent in the studies of the reaction of chlorine oxides.[6] Knowledge of the reactivity of this compound with ionic species is of interest in the context of developing a more complete understanding of the mechanisms of these various reactions.

Experimental Section

All experiments were carried out with a temperature variable fast flow-tube (FT) apparatus. The details of this instrument and the experimental procedure have been described in previous publications,[7] and only a brief outline is presented here. The reactant ions, $NO_2^-\cdot(D_2O)_{n=0-2}$ and $NO_3^-\cdot(D_2O)_{n=0-2}$, were produced by discharge ionization in a flow-tube ion source using He as the buffer gas. Various source gases were added to the ion source to produce desired reactant ion(s). When air (passed through a liquid N_2 trap) was added, almost single NO_2^- ion was produced at room temperature (see inset of Figure 2). To form $NO_2^-\cdot(D_2O)_{n=1,2}$ at lower temperatures, a small amount of D_2O was also added. The $NO_3^-\cdot(D_2O)_{n=0-2}$ ions, together with $NO_2^-(D_2O)_{n=0-2}$, were created when trace amounts of O_2 were added to an air/D_2O/He mixture. A small amount of Cl_2 with O_2 was used as a source of Cl^-. To produce the hydrates, $Cl^-\cdot(D_2O)_{n=1,2}$, D_2O was added.

It should be mentioned that in the NO_2^-/Cl_2O case some measurements showed the intensities of product ions to be much higher than that of reactant ion, NO_2^-. This is probably due to the presence of free electrons which could emerge from the ion source into the FT and react with Cl_2O. An earlier study[8] indicates that thermal-energy electrons quite efficiently react with Cl_2O ($k = 2.6 \times 10^{-10}$ cm^3/s). In the experiments described here, this effect was eliminated by localization of the discharge to a small area and/or the presence in the ion source of trace amounts of electron scavengers such as Cl_2, CCl_4, or water. The relative intensities of the reactant ions could be varied by changing the source gas composition and ion source and FT temperature. After formation, the ions were carried out by He from the ion source into the FT, where they react with preselected concentrations of Cl_2O. The precursor and product ions were mass analyzed by scanning the quadrupole mass spectrometer, and ions were detected with a channeltron electron multiplier. The reaction rate constants were measured in the usual way from the slope of the relative decrease in reactant ion intensity with increasing Cl_2O flow rate, using ion velocity values directly determined in pulsing experiments as described earlier.[7a] Typical operating conditions encompassed a total FT gas pressure of about 0.30 Torr, a buffer gas (He) flow rate of 8×10^3 sccm, and FT temperatures ranging from 168 to 298 K. The FT temperature was controlled within an accuracy of ±1 °C.

[†] This paper is dedicated to Z. Herman on the occasion of his 60th birthday.

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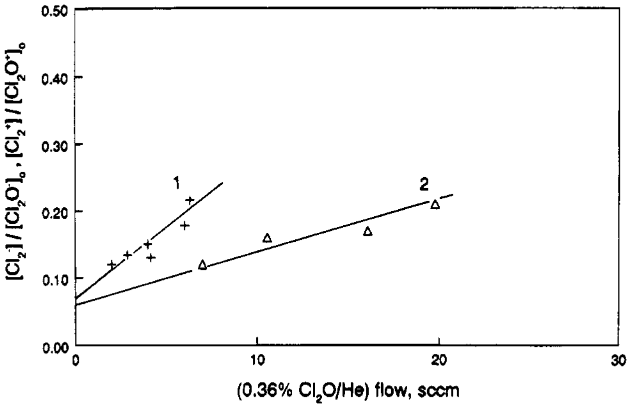


Figure 1. Plot of the ratio (1) $[Cl_2^-]/[Cl_2O^-]_0$ and (2) $[Cl_2^+]/[Cl_2O^+]_0$ *vs* the flow rate of the 0.36% Cl_2O/He mixture at temperatures 208 and 298 K, respectively.

The Cl_2O was prepared by the method of Cady[8] in which $Cl_2(g)$ and air are allowed to react with HgO. Precautions are taken to prevent water from entering the reaction vessel, but to ensure its absence, P_2O_5 was used to remove any that may have been present. The Cl_2O samples were stored in the dark at liquid nitrogen temperatures to prevent decomposition. The samples were additionally purified before each experiment by repeated freeze–thaw cycles and evacuating the sample at −118 °C (liquid N_2/ethanol slush) to remove volatile impurities such as Cl_2; this step was done in the dark to prevent photolysis. The mixture of Cl_2O with He (typically ~0.4% Cl_2O/He) was prepared by introducing Cl_2O into one of 4-L stainless steel reservoirs and adding an appropriate amount of dry He. To obtain homogeneity, the mixture was also introduced into the second 4-L stainless steel reservoir. During the course of the measurements, the Cl_2O/He mixture in both reservoirs was maintained at 0 °C using an ice bath. A MKS Baratron capacitance manometer was used to measure the partial and total pressures of the gases. From both reservoirs, the Cl_2O/He mixture was introduced into the FT through a temperature-controlled stainless steel reactant gas inlet (RGI). The flow rate of the mixture was controlled with a MKS flowmeter. Some experiments were also done using a Teflon RGI. The rate constants measured with both RGIs remained within experimental uncertainties.

The purity of Cl_2O in the FT was estimated by measuring the ratios of $[Cl_2^+]/[Cl_2O^+]_0$ and $[Cl_2^-]/[Cl_2O^-]_0$ *vs* flow rate of the Cl_2O/He mixture (in the range of low flow rates), which upon extrapolation to zero flow rate yielded the initial ion intensity ratios for $[Cl_2^\pm]/[Cl_2O^\pm]$ free from further reactions. Here the values for $[Cl_2O^+]_0$ and $[Cl_2O^-]_0$ include the measured intensities of Cl_2O^+ and Cl_2O^- and their products, respectively, with the exception of contributions to $Cl_2^\pm$ from secondary reactions. The $[Cl_2^+]/[Cl_2O^+]_0$ ratio was determined from the positive ion mass spectra obtained in the charge-transfer reaction of O_2^+ with $Cl_2O + Cl_2$ impurity. The ionization potential of O_2 (12.071 eV) is higher than those of Cl_2O (10.94 eV) and Cl_2 (11.48 eV), but lower than an appearance potential of Cl_2^+ from Cl_2O (≥13.3 eV). The values for $[Cl_2^-]/[Cl_2O^-]_0$ were estimated from the mass spectra taken from the $NO_2^-/(Cl_2O + Cl_2$ impurity) reaction discussed below. As can be seen in Figure 1, at zero flow rate the ion ratios $[Cl_2^+]/[Cl_2O^+]_0$ and $[Cl_2^-]/[Cl_2O^-]_0$ approach about 0.06 and 0.07, respectively. On the basis of these values, using the rate constant values for the reactions O_2^+/Cl_2O ($k = 1.8 \times 10^{-9}$ cm³/s), O_2^+/Cl_2 ($k = 1.1 \times 10^{-9}$ cm³/s), NO_2^-/Cl_2O ($k = 1.6 \times 10^{-9}$ cm³/s), and NO_2^-/Cl_2 ($k = 1.1 \times 10^{-9}$ cm³/s) as determined in this study, Cl_2 impurity in Cl_2O introduced into the flow tube was estimated to be about 9%. To test the stability of Cl_2O in the reservoirs, time dependence measurements of the $[Cl_2^-]/[Cl_2O^-]$ ratio from the NO_2^-/Cl_2O reaction were performed with a 0.36% Cl_2O/He mixture introduced from both reservoirs into the FT at room temperature. The ratio of the monitored intensities at a 10 sccm flow rate, and for times up to 90 min, remained constant within experimental error (Table 1), suggesting that there is no significant decomposition of Cl_2O within this period. All these observations have been taken into consideration for the measurements reported in the present study. An absolute uncertainty in the values of the derived rate constants may be as high as 40% due to uncertainty in the Cl_2O concentration.

TABLE 1: Time Dependence of the $[Cl_2^-]/[Cl_2O^-]$ Ion Ratio[a] from the NO_2^-/Cl_2O Reaction in a 0.36% Cl_2O/He Mixture at Room Temperature (Ion Intensities Monitored at 10 sccm Flow Rate of the Mixture)

time after mixture preparation, min	$[Cl_2^-]/[Cl_2O^-]$
1	0.28 ± 0.05
12	0.28 ± 0.06
27	0.23 ± 0.07
43	0.26 ± 0.06
66	0.32 ± 0.02
97	0.28 ± 0.06
132	0.34 ± 0.05
160	0.43 ± 0.07
190	0.40 ± 0.03

[a] The ratio values are an average of three measurements.

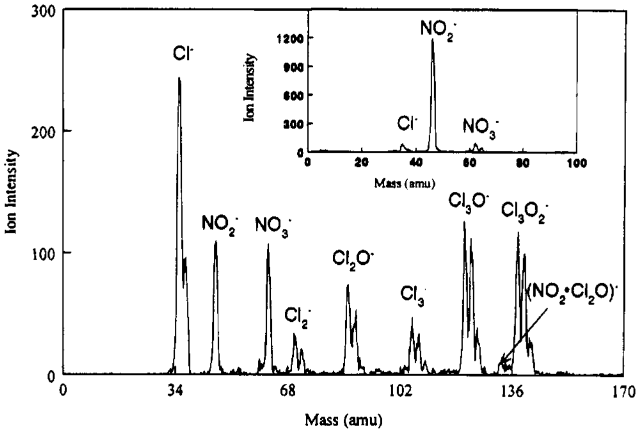


Figure 2. Mass spectra obtained before (inset) and after addition of 81 sccm of a 0.35% Cl_2O/He mixture into the flow tube at room temperature and a flow-tube pressure of 0.27 Torr.

Chemicals. He (Airco, 99.5%), Cl_2 (Matheson, 99.99%), and O_2 (Linde, 99.9%) were used without further purification.

Results and Discussion

$NO_2^- \cdot (D_2O)_{n=0-2}$. Figure 2 displays the mass spectra of the reactant ion, NO_2^- (see inset), and product ions observed at room temperature. Figure 3 shows the sequential chemistry initiated by the NO_2^-/Cl_2O reaction at a temperature of 205 K. Two major ions, Cl_2O^- and Cl^-, are formed from the primary NO_2^-/Cl_2O reaction (a small amount of NO_3^- as well as a trace amount of $(NO_2 \cdot Cl_2O)^-$ is present). The other major ion products observed in the NO_2^-/Cl_2O systems, i.e. Cl_2^-, Cl_3^-, Cl_3O^-, and $Cl_3O_2^-$, are formed in further steps of sequential reactions. (Note that the NO_2^-/Cl_2 reaction pathway to $Cl^- + Cl + NO_2$ is endothermic by ~28 kcal/mol and is not observed.)

The detection of Cl_2O^- and Cl^- in the thermal NO_2^-/Cl_2O reaction indicates that the electron affinity of Cl_2O must be higher than that of NO_2^-; $EA(Cl_2O) > EA(NO_2) = 2.38 \pm 0.06$ eV.[10] This is in line with the value $EA(Cl_2O) \geq 2.53$ eV derived from the heat of formation $\Delta H_f°(Cl_2O^-) \leq -39.2$ kcal/mol.[11] As will be shown below, Cl^- does not charge transfer to Cl_2O.

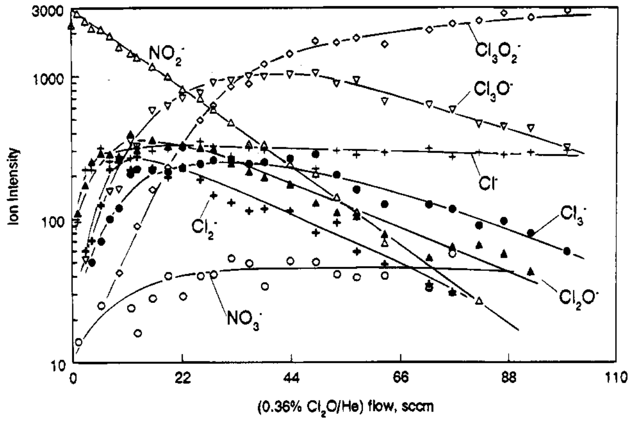
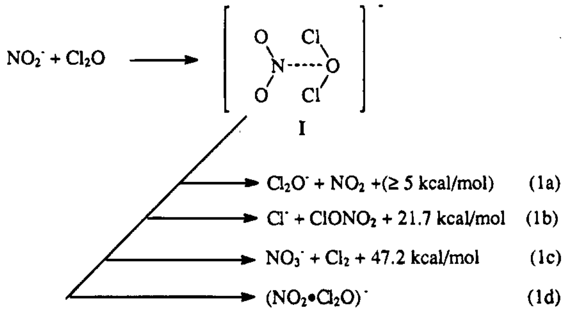


Figure 3. Observed variation of ion signals recorded for the addition of a 0.36% Cl_2O/He mixture into the flow tube in which NO_2^- has been established as the dominant ion in helium buffer gas. $P = 0.28$ Torr and $T = 205$ K.

SCHEME 1



These observations place limits on the electron affinity of Cl_2O: 2.53 eV $\leq$ EA(Cl_2O) $\leq$ 3.617 eV.[12] The four channels are shown in Scheme 1 for the primary NO_2^-/Cl_2O reaction, on the basis of the observed ionic products (Figures 2 and 3) and a thermochemical analysis. The neutral products are not observable in the present experiments, but are deduced from the mass balance and the thermochemical information.[12] The intermediate structure **I** proposed is supported by work[13] showing that in neutral Cl_2O the partial positive charge is on the chlorine atoms. In addition, an *ab initio* study[14] of $NO_2^-\cdot(H_2O)_{n=0-2}$ indicates that negative charge is concentrated on the oxygen atoms.

The neutral product in reaction 1b is most likely $ClONO_2$ rather than $ClO + NO_2$, $ClO_2 + NO$, or $Cl + NO_3$. Dissociation into these otherwise conceivable products requires more energy (4.3, 16.7, and 17.5 kcal/mol, respectively) than is available from the reaction. As seen from Figure 3, NO_3^- maybe a minor ionic product of the NO_2^-/Cl_2O reaction (less than 5%). A reasonable interpretation of the low yield of NO_3^- would be that formation of this ion requires breaking of two Cl−O bonds and formation of a O_2N-O bond, a rearrangement which probably requires a significant activation energy.

For the NO_2^-/Cl_2O system, besides the reaction pathways 1a−1c, the route to $Cl_2^- + NO_3$ is also energetically allowed, but as the electron affinity of NO_3 (3.92 eV) is significantly greater than that of Cl_2 (2.46 eV), pathway 1c is presumably favored. For this reason the route to $Cl_2^- + NO_3$ is not included in Scheme 1.

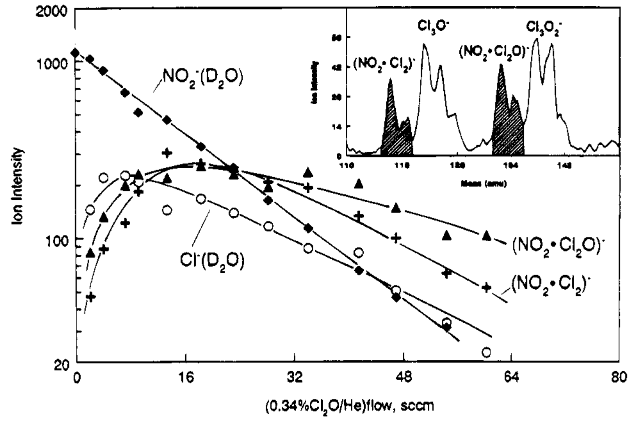
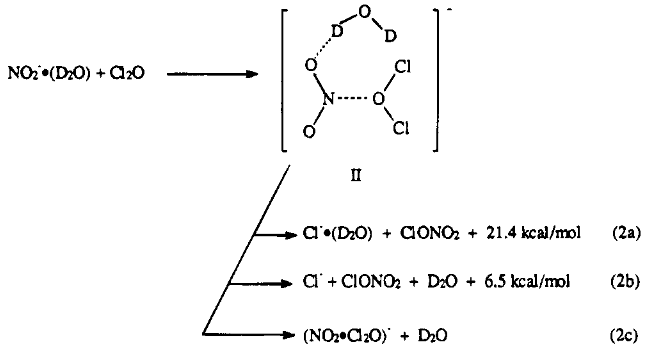
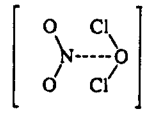


Figure 4. Observed variation of ion signals recorded for the addition of a 0.34% Cl_2O/He mixture into the flow tube in which $NO_2^-\cdot(D_2O)_{n=0,1}$ has been established as the dominant ions in helium buffer gas. $P = 0.32$ Torr and $T = 175$ K.

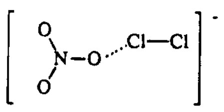
SCHEME 2



With both NO_2^- and $NO_2^-\cdot D_2O$ present as ionic reactants, significant amounts of $Cl^-\cdot D_2O$, $(NO_2\cdot Cl_2)^-$, and $(NO_2\cdot Cl_2O)^-$ are observed as product ions (see Figure 4), in addition to those found under similar conditions for the NO_2^-/Cl_2O system discussed above. The $Cl^-\cdot D_2O$ and $(NO_2\cdot Cl_2O)^-$ ion products could be formed in the $NO_2^-\cdot D_2O/Cl_2O$ reaction by the mechanisms shown in Scheme 2. As was the case with the analogous reaction 1b, the neutral product of pathway 2a is most likely $ClONO_2$; dissociation into $ClO + NO_2$, $ClO_2 + NO$, or $Cl + NO_3$ is estimated to be endothermic by 4.6, 17.1, and 17.9 kcal/mol, respectively. Reaction 2b is energetically feasible, but due to the presence of Cl^- resulting from channel 1b, it could not be experimentally proven under the present experimental conditions. Reaction pathway 2c could be attributed to a ligand-switching reaction, where Cl_2O reacts to displace D_2O from $NO_2^-\cdot D_2O$ to form structure **III**. It is possible, however, that intermediate **II** can lead to structure **IV**. *Ab initio* calculations of Okumura and co-workers[15] predict that structure **IV** is the most stable configuration of the $NO_3^-\cdot Cl_2$ system in which charge is mostly located on the oxygen atoms of NO_3^-. Structure **IV** has been proposed by these authors as the intermediate for the $Cl^- + ClONO_2 \Rightarrow Cl_2 + NO_3^-$ reaction, but not observed experimentally with their FT-ICR apparatus at pressures of (1−4) × 10^{-7} Torr. However, the failure to observe the $NO_3^-\cdot Cl_2$ complex by Okumura and co-workers could be due to the lack of collisional stabilization under low-pressure conditions. The question, therefore, arises whether the ion products from the $NO_2^-\cdot(D_2O)/Cl_2O$ and $Cl^-/ClONO_2$ reactions have the same or different structures. The answer comes from our separate FT study,[16] showing that not even a trace amount of the complex $(NO_3\cdot Cl_2)^-$ from the $Cl^-/ClONO_2$ reaction is observed at temperatures of 165−210 K; the primary



III



IV

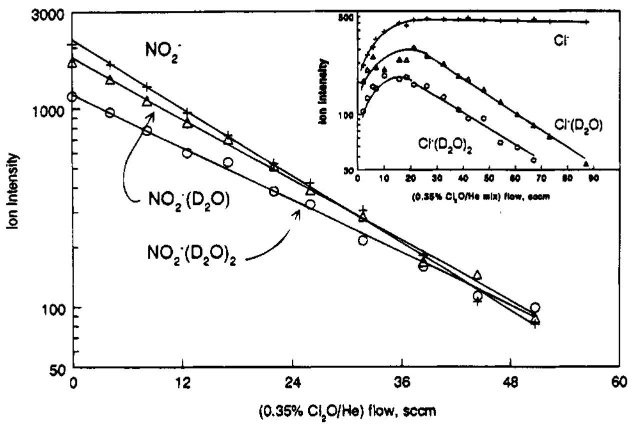
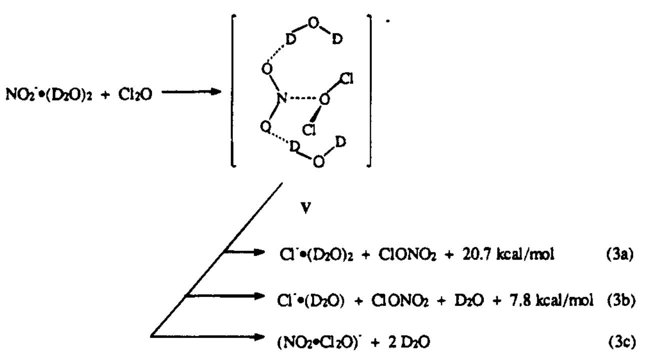


Figure 5. Observed variation of ion signals recorded for the addition of a 0.35% Cl_2O/He mixture into the flow tube in which $NO_2^-\cdot(D_2O)_{n=0-2}$ has been established as the dominant ions in helium buffer gas. The inset shows the variation of the $Cl^-\cdot(D_2O)_{n=0-2}$ product ion signals for the reactions of $NO_2^-\cdot(D_2O)_{n=0-2}$ with Cl_2O. $P = 0.32$ Torr and $T = 184$ K.

SCHEME 3



ionic product found is NO_3^-. This observation, together with our findings of the behavior under similar conditions of $(NO_2\cdot Cl_2O)^-$ from $NO_2^-\cdot(D_2O)/Cl_2O$, strongly suggests that the reaction pathway 2c does not lead to structure **IV**, but most probably to **III**.

The observation of this reaction places a lower limit on bond energy $D(NO_2-Cl_2O)^- > D(NO_2^- -D_2O) = 15.2$ kcal/mol and an upper limit $\Delta H_f°(NO_2\cdot Cl_2O)^- < -41.4$ kcal/mol. The formation of $(NO_2\cdot Cl_2)^-$ can be attributed, at least in part, to the reaction of $NO_2^-\cdot D_2O$ with Cl_2 which is present as an impurity in the system specified. In separate experiments[16] we found that the $NO_2^-\cdot D_2O/Cl_2$ reaction yields $(NO_2\cdot Cl_2)^- + D_2O$. In the present study we cannot, however, totally exclude the possibility that $(NO_2\cdot Cl_2)^-$ is also formed from the $NO_2^-\cdot D_2O + Cl_2O \rightarrow (NO_2\cdot Cl_2)^- + D_2O_2$ reaction.

As can be seen from Figure 5, when $NO_2^-\cdot(D_2O)_{n=0-2}$ is allowed to react, $Cl^-\cdot(D_2O)_{n=0-2}$ are formed. Also, at higher flow rates the intensities of both hydrated ion products, $Cl^-\cdot(D_2O)_{n=1,2}$, decrease rapidly with addition of Cl_2O. The observation of $Cl^-\cdot(D_2O)_2$ in these experiments indicates that an electron and two water ligands are simultaneously transferred from $NO_2^-\cdot(D_2O)_2$ to Cl in the $NO_2^-\cdot(D_2O)_2/Cl_2O$ reaction. A possible mechanism is that the Cl atoms receive charge during the initial interaction as the $[NO_2^-\cdot(D_2O)_2\cdots ClOCl]$ intermediate adduct is formed, so that the positively charged D atoms attack one of the Cl atoms (Scheme 3). One might expect the rearrangement involves the reorientation of water ligands about the new charge distribution and bond reorganization within the intermediate, as well as formation of a transition state for dissociation into the products $Cl^-\cdot(D_2O)_2 + ClONO_2$.

Analyzing the reactant, $NO_2^-\cdot(D_2O)_2$, and product, $Cl^-\cdot(D_2O)_2$, ion intensities at low flow rates shows that pathway 3a is the predominant process of the $NO_2^-\cdot(D_2O)_2/Cl_2O$ reaction. This pathway is obviously thermochemically favored on energetic grounds. Confirmation of reaction pathways 3b and 3c could not be made in the present experiments because $Cl^-\cdot(D_2O)$ and $(NO_2\cdot Cl_2O)^-$ also are simultaneously produced from $NO_2^-\cdot(D_2O)/Cl_2O$ (see Scheme 2). Of interest is the fact that despite the complex mechanism, the $NO_2^-\cdot(D_2O)_2/Cl_2O$ reaction occurs at the collision rate (Table 2). This suggests that the dynamics of the intramolecular rearrangement within intermediate **V** is fast compared with the dissociation process for product formation.

TABLE 2: Rate Constants[a] for the Reactions of Cl_2O with $NO_2^-\cdot(D_2O)_{n=0-2}$ at Several Temperatures

n	k_{exp}	k_{cal}[b]	T (K)
0	1.56 ± 0.06	1.49	298
	1.63 ± 0.09	1.56	211
	1.69 ± 0.04	1.58	184
	1.63 ± 0.02	1.59	175
	1.66 ± 0.09	1.60	168
1	1.60 ± 0.14	1.40	211
	1.51 ± 0.09	1.42	184
	1.55 ± 0.02	1.43	175
	1.56 ± 0.02	1.44	168
2	1.38 ± 0.05	1.32	184
	1.20 ± 0.11	1.33	175
	1.47 ± 0.12	1.34	168

[a] Units for all rate constants are 10^{-9} cm³/s. [b] Collision rates were calculated from the Su–Chesnavich theory[17] using $\alpha(Cl_2O) = 9.1$ Å³ and $\mu_D = 0.78$ D.[18]

TABLE 3: Rate Constants[a] for the Reactions of Cl_2O with $Cl^-\cdot(D_2O)_{n=0-2}$ at a Temperature of 215 K

n	k_{exp}	k_{cal}[b]
0	0.036 ± 0.012	1.71
1	1.47 ± 0.05	1.47
2	1.48 ± 0.05	1.34

[a] Units for all rate constants are 10^{-9} cm³/s. [b] Collision rates were calculated from the Su–Chesnavich theory.[17]

Two other possible reactions related to Schemes 2 and 3 need to be considered. A charge-transfer process (reaction 4a) would be endothermic (≥10 kcal/mol) if $\Delta H_f°(Cl_2O^-) = -39.2$ kcal/mol.[11]

$$NO_2^-\cdot(D_2O)_{n=1,2} + Cl_2O \rightarrow Cl_2O^- + nD_2O + NO_2 \quad (4a)$$

Another, namely, reaction 4b is probably exothermic.

$$NO_2^-\cdot(D_2O)_{n=1,2} + Cl_2O \rightarrow Cl_2O^-\cdot(D_2O)_m + (n-m)D_2O + NO_2 \quad (4b)$$

However, we cannot confirm its occurrence due to interference of large peaks, from Cl_3^- and Cl_3O^- formed in secondary reactions. However, analysis of the ion intensities of reactant and product ions involved in reactions 2 and 3 suggests that reaction 4b, if it occurs, is much less efficient than (2) and (3).

Table 2 provides the rate constants determined for the reactions of $NO_2^-\cdot(D_2O)_{n=0-2}$ with Cl_2O at several temperatures. In every case these values, as well as those given in Tables 3 and 4, are an average of at least five measurements, and the error limits show the statistical fluctuations. The calculated collision rate constants from the Su–Chesnavich theory,[17] using $\alpha_{Cl_2O} = 9.1$ Å³ and $\mu_D = 0.78$ D,[18] are also given in Table 2. Comparison between the calculations and the experimental results indicates that in the gas phase the $NO_2^-\cdot(D_2O)_{n=0-2}$ ions react with Cl_2O at the collisional rate. This implies that there is little or no activation barrier for these reactions. Almost all ion products arising from the primary $NO_2^-\cdot(D_2O)_{n=0-2}/Cl_2O$

TABLE 4: Rate Constants[a] for the Reactions of Cl_2O with $NO_3^-\cdot(D_2O)_{n=0-2}$ at a Temperature of 184 K

n	k_{exp}	k_{cal}[b]
0	0.056 ± 0.012	1.44
1	0.55 ± 0.05	1.34
2	0.52 ± 0.09	1.27

[a] Units for all rate constants are 10^{-9} cm^3/s. [b] Collision rates were calculated from the Su–Chesnavich theory.[17]

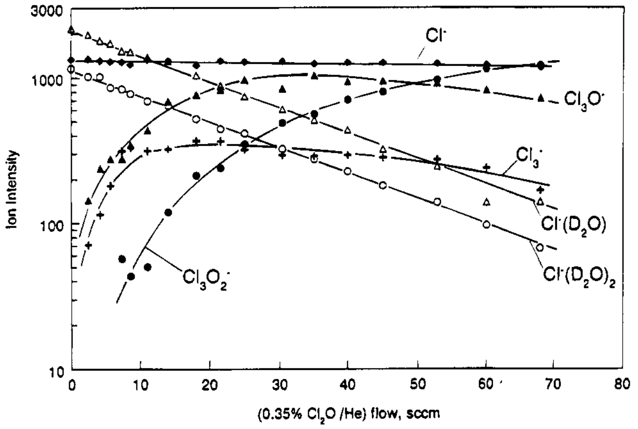


Figure 6. Observed variation of ion signals recorded for the addition of a 0.35% Cl_2O/He mixture into the flow tube in which $Cl^-\cdot(D_2O)_{n=0-2}$ has been established as the dominant ions in the helium buffer gas. P = 0.30 Torr and T = 215 K.

reactions were observed to react efficiently with Cl_2O. A detailed discussion of reactions of these ions follows.

$Cl^-\cdot(D_2O)_{n=0-2}$. As can be seen in the inset of Figure 5, in contrast to Cl^-, both hydrated chloride ions, $Cl^-\cdot(D_2O)_{n=1,2}$, efficiently react with Cl_2O. When $Cl^-\cdot(D_2O)_{n=0-2}$ are prepared as reactants in the ion source and are allowed to react with Cl_2O in the FT, the behavior (Figure 6) of these ions is very similar to that shown in Figure 5. The results in Figure 6 also show the product ions formed in the $Cl^-\cdot(D_2O)_{n=0-2}/Cl_2O$ reactions. These are the same products we observed for the $Cl^-\cdot(D_2O)_{n=0,1}/Cl_2O$ systems with only a higher ratio of the relative intensities of Cl_3^-/Cl_3O^-. It is worthwhile pointing out that for the Cl^-/Cl_2O reaction the ion products, if present, were within the noise level. This is consistent with the small rate constant found for this reaction (Table 3). In addition to these results, in separate experiments[16] we found that the $Cl^-\cdot D_2O + Cl_2 \rightarrow Cl_3^- + D_2O$ reaction occurs at the collision rate ($k = 0.92 \times 10^{-9}$ cm^3/s), while that of Cl^-/Cl_2 is very slow, which is consistent with a previous study[19] of this system ($k = (2.7-5.2) \times 10^{-13}$ cm^3/s). The observed intensity of the Cl_3^- ion in the $Cl^-\cdot(D_2O)_{n=0,1}/Cl_2O$ and $Cl^-\cdot(D_2O)_{n=0-2}/Cl_2O$ systems is much higher than it might be expected from the impurity of Cl_2 in Cl_2O, which suggests that Cl_3^- is also formed from $Cl^-\cdot(D_2O)_{n=1,2}/Cl_2O$. Summing up all these observations, the following scheme is postulated for the reactions of $Cl^-\cdot(D_2O)_{n=0-2}$ with Cl_2O.

$$Cl^- + Cl_2O \leftrightarrow [Cl_3O^-]^* \rightarrow \text{products} \qquad (5)$$

$$Cl^-\cdot(D_2O)_{n=1,2} + Cl_2O \rightarrow Cl_3O^- + nD_2O \qquad (6a)$$

$$\rightarrow Cl_3^- + D_2O_2 + (n-1)D_2O \qquad (6b)$$

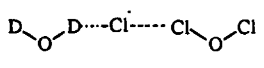
$$Cl_3^- + Cl_2O \rightarrow Cl_3O^- + Cl_2 \qquad (7)$$

$$Cl_3O^- + Cl_2O \rightarrow Cl_3O_2^- + Cl_2 \qquad (8)$$

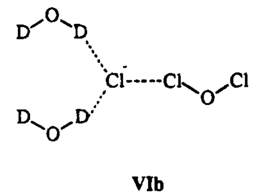
Reaction 5 would lead to the excited association complex, $[Cl_3O^-]^*$, which then might either dissociate into the reaction products and/or back to the reactants or be stabilized by third-body collisions. The absence of Cl_3O^- and other ionic products in the Cl^-/Cl_2O reaction indicates that, under the present experimental conditions, the collisional stabilization of $[Cl_3O^-]^*$ is not effective. Moreover, thermochemical information indicates that indeed all routes to eventual products of reaction 5, i.e., $Cl_2^- + ClO$, $ClO^- + Cl_2$, $Cl_2O^- + Cl$, $Cl_3^- + O$, and $O^- + Cl_3$, are endothermic, so that any $[Cl_3O^-]^*$ would dissociate to the reactants, $Cl^- + Cl_2O$.

For the $Cl^-(D_2O)_2/Cl_2O$ system, using the lower literature value[20] for $\Delta H_f°(Cl_3^-) = -82.8$ kcal/mol shows that the reaction pathway 6b is endothermic by 5 kcal/mol. This means that the reaction of $Cl^-\cdot(D_2O)_2$ with Cl_2O occurs only via channel 6a, indicating that this channel is exothermic or nearly so and placing a limit on $\Delta H_f°(Cl_3O^-) \leq -63$ kcal/mol. This limit yields a bond energy $D(Cl^- - Cl_2O) \geq 27.8$ kcal/mol, which will also be used for thermochemical analysis of other reactions discussed in the present work.

As is evident from Table 3, the $Cl^-\cdot(D_2O)_{n=1,2}/Cl_2O$ reactions are collisional. These reactions probably proceed by an initial attack of the negatively charged chloride in $Cl^-\cdot(D_2O)_{n=1,2}$ on one of the Cl atoms of Cl_2O to form intermediate structures like **VIa** and **VIb**. From these structures, Cl_3O^- can be easily formed by a simple nucleophilic displacement mechanism. However, formation of Cl_3^- in the $Cl^-\cdot(D_2O)/Cl_2O$ reaction (channel 6b) is obviously not accessible without considerable rearrangement of structure **VIa**.



VIa



VIb

Cl_2O^-. As discussed above, without hydration the Cl^-/Cl_2O system does not give any measurable ion products. Also, NO_3^- was observed to react with Cl_2O very slowly, yielding $NO_3^-\cdot Cl_2O$, as described below. On the basis of these facts, the Cl^- and NO_3^- ions, which arise from the primary NO_2^-/Cl_2O reaction can be excluded from possible secondary reactions leading to ionic products (Figures 2 and 3) of the NO_2^-/Cl_2O system. Therefore, Cl_2O^- is the only candidate to take part in secondary reactions with Cl_2O. From the normalized intensities of the ions involved in secondary and further reactions (Figure 7) obtained from the raw data shown in Figure 3, it is clear that the major ion product formed from the Cl_2O^-/Cl_2O reaction is Cl_2^-. The most likely route to this ion is by nucleophilic attack of Cl_2O^- on the oxygen atom of a neutral partner, followed by elimination of Cl_2O_2 (pathway 9a) (Scheme 4). The lower limit of the rate constant ($k = 0.9 \times 10^{-9}$ cm^3/s) for the Cl_2O^-/Cl_2O system derived from secondary reaction is close to the collision rate ($k_{cal} = 1.3 \times 10^{-9}$ cm^3/s[17]). This observation indicates that the Cl_2O^-/Cl_2O reaction occurs quite easily and suggests that there is no substantial barrier to the formation of products. The route to $Cl_3^- + ClO_2$ is also exothermic. However, it is hard to imagine formation of these products without considerable rearrangement of intermediate **VII**. Therefore, channel 9b should be a kinetically less favored process than channel 9a. Also, intermediate **VII** cannot lead directly to the $Cl_3O^- + ClO$ products (channel 9c), and this route most likely is less exothermic than (9a), so that pathway 9a should be favored.

Of course, in the present experiments (without using the SIFT arrangement) we cannot fully exclude product formation via

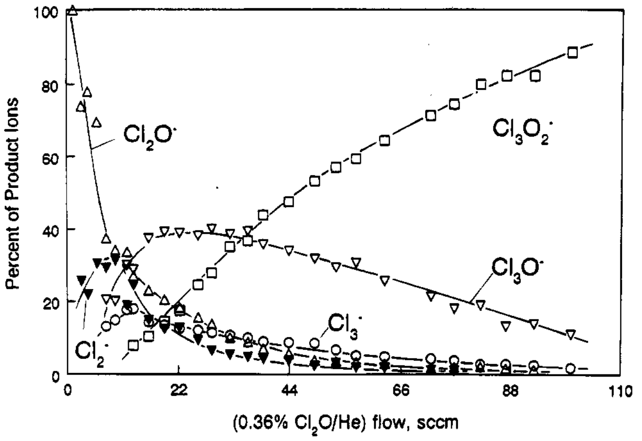
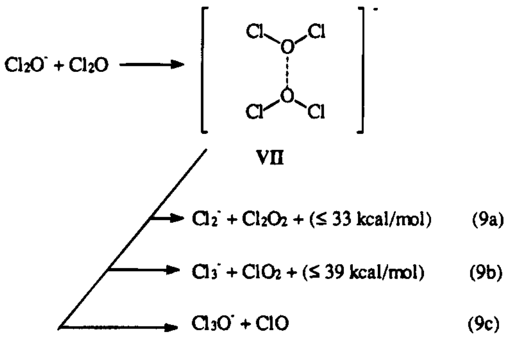


Figure 7. Normalized intensities of product ions for the reaction of NO_2^- with Cl_2O as a function of the (0.36% Cl_2O/He) mixture flow rate. The Cl^- and NO_3^- ions are excluded (see explanation in the text). As a reference, the decay of NO_2^- with the addition of the Cl_2O/He mixture under the same experimental conditions is given in Figure 2. $P = 0.28$ Torr and $T = 205$ K.

SCHEME 4



the reaction channels 9b and 9c. However, if these reactions occur, their efficiencies are probably significantly lower than (9a).

$(NO_2 \cdot Cl_2)^-$. The $(NO_2 \cdot Cl_2)^-$ ion was observed to react further with Cl_2O (Figure 4). However, the nature of further reaction(s) of this species is not clear. The following pathways,

$$(NO_2 \cdot Cl_2)^- + Cl_2O \rightarrow Cl_3^- + ClONO_2 \qquad (10a)$$

$$\rightarrow NO_3^- + 2Cl_2 \qquad (10b)$$

are exothermic (by about 28 and 25 kcal/mol, respectively) with $\Delta H_f^\circ(Cl_3^-) = -82.8$ kcal/mol,[20] and $\Delta H_f^\circ(NO_2 \cdot Cl_2)^- \approx -67$ kcal/mol, as derived from thermochemical data, assuming that the bond energy $D(NO_2-Cl_2)^- \approx 18$ kcal/mol. However, from the present experiments, confirmation of these reaction pathways is difficult because the same ion products are formed in other reactions.

$(NO_2 \cdot Cl_2O)^-$. As discussed above, the $(NO_2 \cdot Cl_2O)^-$ ion is formed from $NO_2^- \cdot (D_2O)/Cl_2O$ (see Scheme 2) and under our FT conditions is a long-lived species. This species is a little less reactive than $(NO_2 \cdot Cl_2)^-$; its reactivity is visible at high flow rates (Figure 4). The possibile reaction for this ion is shown in Scheme 5. This reaction is probably exothermic; the upper limits for $\Delta H_f^\circ(NO_2 \cdot Cl_2O)^- < -41.2$ kcal/mol and $\Delta H_f^\circ(Cl_3O^-) < -63$ kcal/mol indicate a reaction exothermicity by about 35 kcal/mol. However, due to the presence of Cl_3O^- from other reactions, it could not be experimentally proven in the present experiments.

Cl_2^-. As can be seen in Figure 7, Cl_2^- reacts rapidly with Cl_2O. The exothermic pathway 12a and 12b, which can lead directly to ion products, Cl_3^- and Cl_2O^-, through the intermediate **IX**, seems to be the most likely reaction mechanism of the Cl_2^-/Cl_2O system (Scheme 6). This transition-state structure is consistent with the observation that the Cl_2^-/Cl_2O reaction occurs efficiently, as is suggested by the lower limit of the rate constant ($k = 1.1 \times 10^{-9}$ cm^3/s), obtained from secondary reaction, with a near collisional rate at 205 K ($k_{cal} = 1.37 \times 10^{-9}$ cm^3/s[17]). Reaction channel 12c is slightly endothermic, but due to some uncertainty in the Cl_3O^- heat of formation, this channel cannot be ruled out on the basis of the thermochemical analysis. The Cl_2^-/Cl_2O reaction pathway to Cl^- + Cl_3O can be excluded because of lack of contribution to the Cl^- signal.

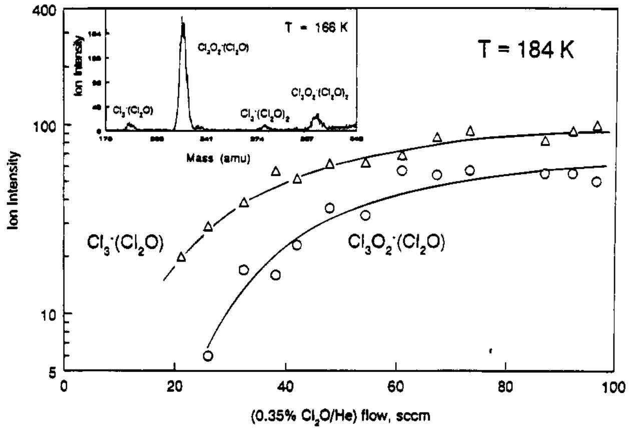
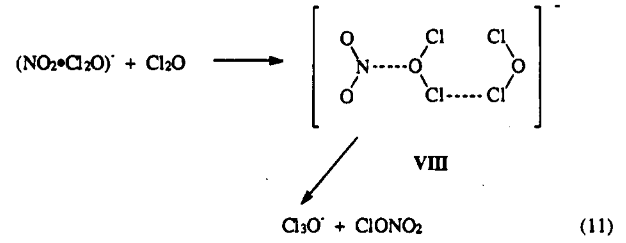
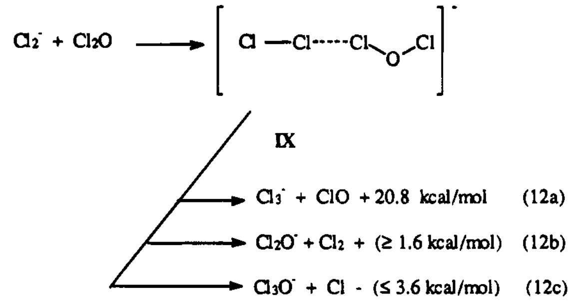


Figure 8. Observed variation of the $Cl_3^- \cdot (Cl_2O)$ and $Cl_3O_2^- \cdot (Cl_2O)$ ion signals recorded for the addition of a 0.35% Cl_2O/He mixture into the flow tube at $T = 184$ K and $P = 0.32$ Torr. The formation of precursors of these ion is shown in Figure 6. The inset displays the region of the mass spectrum showing the $Cl_3^- \cdot (Cl_2O)_{n=1,2}$ and $Cl_3O_2^- \cdot (Cl_2O)_{n=1,2}$ adduct ions at $T = 166$ K and a flow-tube pressure of 0.30 Torr.

SCHEME 5



SCHEME 6



Cl_3^-. The Cl_3^- ion was observed (Figures 6 and 7) to react further with Cl_2O. The major product ion is Cl_3O^-, but at low temperatures the adduct ions, $Cl_3^- \cdot (Cl_2O)_{n=1,2}$, were also observed (Figure 8). Calculations[21] indicate that the ground state of Cl_3^- is the closed-shell singlet state and has a linear structure in which negative charge is distributed at the terminal atoms. Therefore, it might be expected that the Cl_3^-/Cl_2O reaction proceeds by attack of the terminal chloride of Cl_3^- on

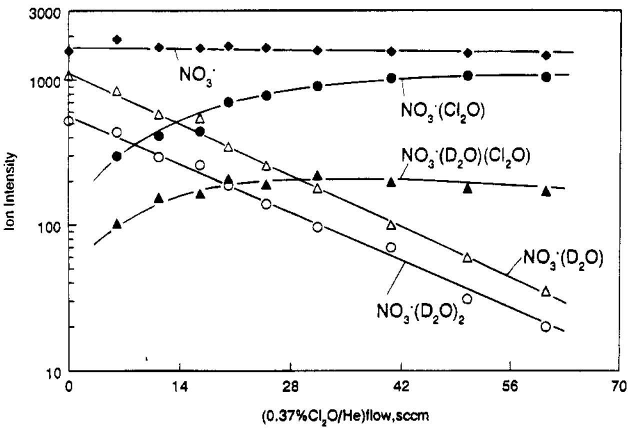
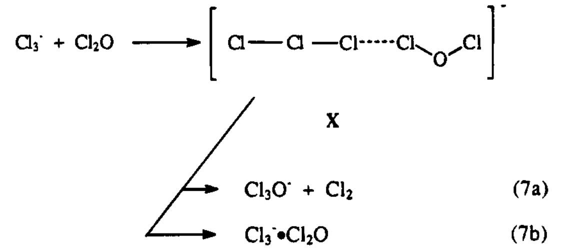


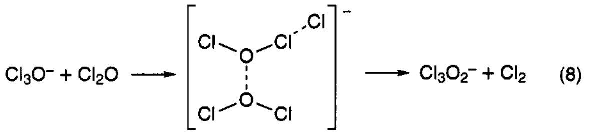
Figure 9. Observed variation of ion signals recorded for the addition of a 0.37% Cl_2O/He mixture into the flow tube in which $NO_3^-{\cdot}(D_2O)_{n=0-2}$ has been established as the dominant ions in helium buffer gas. $P = 0.30$ Torr and $T = 168$ K.

SCHEME 7



one of the Cl atoms in Cl_2O, followed by formation of an intermediate complex similar to **X** which can lead directly to the $Cl_3O^- + Cl_2$ products via Cl–Cl bond fission (channel 7a). We propose that this channel occurs in competition with stabilization of the collision complex by the mechanism shown in Scheme 7. Taking into account the limits for the heat of formation[20] for Cl_3^-, -72.7 kcal/mol $> \Delta H_f°(Cl_3^-) > -82.8$ kcal/mol, the reaction pathway 7a is probably exothermic or thermoneutral.

Cl_3O^-. From Figures 3, 6, and 7 it is evident that Cl_3O^- reacts with Cl_2O to form $Cl_3O_2^-$ (and Cl_2). No signal at *m/e* 207 was detected, which indicates that the $[Cl_3O^-{\cdot}Cl_2O]$ ion–molecule collision complex quickly decomposes in the FT even at the lowest temperatures (168 K). The Cl_3O^-/Cl_2O reaction can be initiated by attack of Cl_2O on the oxygen atom, followed by formation of an intermediate **XI** in which a Cl_2O molecule displaces a Cl_2 molecule to form the product ion, $Cl_3O_2^-$, as shown in reaction 8. This species appears to be quite reactive. At low temperatures, in subsequent collisions with Cl_2O, the adduct ions, $Cl_3O_2^-{\cdot}(Cl_2O)_{n=1,2}$, were observed to be formed (Figure 8) as expressed by reactions 13 and 14.



XI

$$Cl_3O_2^- + Cl_2O \longrightarrow Cl_3O_2^- \bullet Cl_2O \qquad (13)$$

$$Cl_3O_2^- \bullet (Cl_2O) + Cl_2O \longrightarrow Cl_3O_2^- \bullet (Cl_2O)_2 \qquad (14)$$

These reactions are presumably termolecular at the FT conditions, with He acting as the stabilizing gas.

$NO_3^-{\cdot}(D_2O)_{n=0-2}$. As can be seen in Figure 9, NO_3^- reacts slowly with Cl_2O. The only product seen in this reaction is $NO_3^-{\cdot}Cl_2O$, which under our experimental conditions is expected to be formed in termolecular reaction 15.

$$NO_3^- + Cl_2O \leftrightarrow [NO_3^-{\cdot}Cl_2O]^* \xrightarrow{He} NO_3^-{\cdot}Cl_2O \qquad (15)$$

In contrast to NO_3^-, both hydrated ions $NO_3^-{\cdot}(D_2O)_{n=1,2}$ were found to react efficiently (Figure 9) to form $NO_3^-{\cdot}Cl_2O$ and $NO_3^-{\cdot}(D_2O)(Cl_2O)$. (No adduct ion of $NO_3^-{\cdot}(D_2O)_2$ with Cl_2O was observed.) We attribute the formation of these ions to reaction 16

$$NO_3^-{\cdot}(D_2O)_n + Cl_2O \rightarrow NO_3^-{\cdot}(D_2O){\cdot}Cl_2O + (n-1)D_2O \qquad (16)$$

which probably proceeds by a displacement mechanism. The observation of switching reaction 16 suggests that $D(NO_3^- - Cl_2O) > D(NO_3^- - D_2O) = 14.6$ kcal/mol and $D(NO_3^-{\cdot}D_2O - Cl_2O) > D(NO_3^-{\cdot}D_2O - D_2O) = 14.3$ kcal/mol. The rate constants determined for the $NO_3^-{\cdot}(D_2O)_{n=0-2}/Cl_2O$ systems are given in Table 4. As can be seen, the observed rate coefficient, k_{exp}, for NO_3^-/Cl_2O is much smaller than the collision rate, k_{cal}. This presumably is due to low efficiency for stabilization by He of the excited $[NO_3^-{\cdot}Cl_2O)]^*$ complex arising from its short lifetime compared to the collision frequency.

The k_{exp} values for $NO_3^-{\cdot}(D_2O)_{n=1,2}/Cl_2O$ are about 40% of the calculated collision rates. The slower rates observed for these systems may reflect the charge delocalization in the reactant ions. In the studies of the $NO_3^-{\cdot}H_2O/HNO_3$[22] and $NO_3^-{\cdot}(H_2O)_{n=1,2}/N_2O_5$[23] systems, it has also been found that the measured rate constants are significantly smaller than the collision rates.

Conclusions

The reactivity of $NO^-_{x=2,3}{\cdot}(D_2O)_{n=0-2}$ and $Cl^-{\cdot}(D_2O)_{n=0-2}$ with Cl_2O has been accessed. Rich chemistry is found for the reactions of the $NO_2^-{\cdot}(D_2O)_{n=0-2}$ ions, which react with Cl_2O at the gas collision rates. The rate constants determined for these reactions cover a large range of temperature. In this study we have characterized the primary reactions for the studied systems, and we have seen how these reactions may promote the synthesis of chloride-containing species such as Cl_3^-, Cl_3O^-, and $Cl_3O_2^-$. These observations can yield new insight into the ion chemistry of chloride compounds and may be interesting from the mechanistic viewpoint of complex chloride systems and heterogeneous reactions. Current considerations suggest that although Cl_2O is not directly involved in atmospheric chemistry, because of its similarity in structure to such species as the ClO dimer (ClOOCl), which plays an important role in ozone destruction in the polar stratosphere, the ionic reactions reported in this study for Cl_2O may serve for a better mechanistic understanding of heterogeneous chemistry of atmospherically important chloride compounds (ClO, ClOOCl, HOCl).

It is interesting to note that in contrast to Cl^- and NO_3^-, with hydrated ions, $Cl^-{\cdot}(D_2O)_{n=1,2}$ and $NO_3^-{\cdot}(D_2O)_{n=1,2}$, Cl_2O reacts efficiently. It should be also mentioned that similar behavior was observed for the $Cl^-{\cdot}(D_2O)_{n=0,1}/Cl_2$ system. The rapid bimolecular reactions of hydrated ions may be viewed as reactions in which, in a formal sense, water catalyzes the formation of adduct species such as Cl_3^-, Cl_3O^-, and $NO_3^-{\cdot}Cl_2O$ according to the reaction sequence given in reactions 17–19,

$$Cl^-, NO_3^- + H_2O \rightarrow Cl^-\cdot(H_2O), NO_3^-\cdot(H_2O) \quad (17)$$

$$Cl^-\cdot(H_2O), NO_3^-\cdot(H_2O) + Cl_2O, (Cl_2) \rightarrow Cl_3O^-, (Cl_3^-), NO_3^-\cdot Cl_2O + H_2O \quad (18)$$

$$\text{Net: } Cl^-, NO_3^- + Cl_2O, (Cl_2) \rightarrow Cl_3O^-, (Cl_3^-), NO_3^-\cdot Cl_2O \quad (19)$$

which is written without any inferences about structure and mechanism.

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