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Gas phase reactions of Cl_2O with $X^-(D_2O)_{n=0-4}$ ($X = O, OD, O_2, DO_2$, and O_3)

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Abstract

The reactions of Cl_2O with the cluster ions $X^-(D_2O)_{n=0-4}$ ($X = O$, OD, O_2, DO_2, and O_3) were studied in a He buffer gas at temperatures within the range 171–298 K and pressures of 0.27–0.51 Torr, using a flow-tube apparatus. All ions were found to react with Cl_2O at rates slower than predicted by the collision rate and the charge center was transferred from X^- to Cl^- or ClO^-. The primary product ions $Cl^-(DOCl)$ and $ClO^-(DOCl)$ were observed to react further to produce the ions Cl_3O^- and $Cl_3O_2^-$. The rate constants for the observed reactions are reported and the role that thermodynamics plays in determining possible reaction channels is discussed. (Int J Mass Spectrom 182/183 (1999) 31–44) © 1999 Elsevier Science B.V.

Keywords: Gas phase reactions; Cl_2O; $X^-(D_2O)_{n=0-4}$ ($X = O$, OD, O_2, DO_2, and O_3)

1. Introduction

It is well known that heterogeneous reactions occurring on polar stratospheric clouds (PSC's) and stratospheric aerosol particles affect ozone concentrations by converting inert chlorine compounds to species that catalytically destroy ozone [1]. However, the mechanisms by which these surface reactions occur have not been fully elucidated. Recently studies of heterogeneous reactions found that ionic mechanisms and solvation effects may be a key to understanding the reactions that occur on the surfaces or within aerosols and cloud particles [2]. The use of gas phase cluster ions as PSC mimics, allows for exploration into mechanistic details and the importance of solvation effects which are not easily available from experiments that employ bulk surfaces [3]. Additionally, recently it has been proposed that ion sites exist on these atmospheric surfaces [4], formed from dissolved acids such as HCl on the surface. This has prompted several studies from our laboratories including: gas-phase reactions of N_2O_5 with protonated water clusters [5] $H^+(H_2O)_{n=3-30}$, hydrated anions [6] $X^-(H_2O)_{n\leq 5}$, $X = O$, OH, O_2, O_2H, O_3, NO_2 and NO_3, and $NO^-_{n=2,3}$ HNO_2, and the gas-phase reactions of Cl_2O with NO_2^- $(D_2O)_{n=0,1,2}$, $NO_3^-(D_2O)_{n=0,1,2}$ and $Cl^-(D_2O)_{n=0-2}$ [7].

The results of the first study of the reactions of Cl_2O, with the anions $X^-(D_2O)_{n=0-4}$ ($X = O$, OD, O_2, DO_2, and O_3) are presented in this article. The atmospheric concentration of dichlorine monoxide (Cl_2O) is very low [8] (10^{-17} mol cm^{-3}) and this species is not generally included in current atmospheric models. However, studies of the reactivity of

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Dedicated to the memory of Ben Freiser.

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Cl_2O with ionic species serve to contribute to a more complete understanding of the reactions of chlorine oxides, in general, and may help to elucidate some of the general mechanisms of catalytic activity related to heterogeneous reactions of atmospheric importance. The attachment of solvent molecules to an ion can modify both the potential energy surface as well as the collision dynamics, in some cases having a profound influence on the mechanisms and reactivity of the ions. For example, in the presence of water the Cl_2O molecule undergoes the following reaction [9].

$$Cl_2O + H_2O \rightleftharpoons 2\,HOCl \tag{1}$$

In the limit of low water vapor concentrations, equilibrium favors Cl_2O; however, suitable water concentrations promote the formation of HOCl which is an important species in stratospheric ozone chemistry. Ionic species may affect the equilibrium by favoring the forward reaction, possibly creating ion products that are more stable than HOCl. Furthermore, studies of the reactions of Cl_2O may provide valuable insight into the chemistry of other chlorine oxides (e.g. ClO, ClOOCl) which are similar in structure and are believed to be directly responsible for decreases in ozone concentrations [1].

2. Experimental

All experiments were carried out with a variable temperature fast flow-tube (FT) apparatus. Detailed descriptions of the apparatus and experimental procedures are given elsewhere [10]. In brief, the reactant ions $X^-\,(D_2O)_{n=0-4}$ X = O, OD, O_2, DO_2, and O_3 were produced in a high pressure (≈ 20 Torr) ion source by a discharge ionization of a D_2O/He mixture containing a trace amount of O_2. The He carrier gas then transports the ions from the source to the FT, where they react with Cl_2O.

The reactant and product ions are then mass analyzed using a quadrupole mass spectrometer and detected with a channeltron electron multiplier. Rate constants are determined by plotting the logarithmic decrease in reactant ion intensity versus the neutral reactant concentration. Pulsing experiments, described in an earlier study [10a], were used to determine the ion velocity and therefore the reaction times.

Cl_2O was prepared as described by Cady [11], whereby Cl_2 gas is allowed to react with HgO. This sample is then purified using P_2O_5 to remove excess H_2O in order to avoid the formation of HOCl. Removal of volatile impurities such as Cl_2 gas is done by pumping on the sample at −118 °C (EtOH/liquid N_2 slush). All purification steps and sample storage were done in the dark to prevent photolysis.

The Cl_2O sample was diluted with dry He in two 4L stainless steel reservoirs, using an ice bath to keep the mixture at 0 °C. This mixture was then introduced into the FT using a MKS mass flow controller to vary the flow rate and therefore the reactant neutral concentration.

Typical operating conditions were as follows: FT pressure 0.27–0.51 Torr, and FT temperature ranging from 298–171 K, with bulk He carrier gas flow rates of about 7000 sccm (standard cubic centimeters per minute).

3. Results

As can be seen in Figs. 1 and 2, all reactant ions $X^-(D_2O)_{n=0-2}$ X = O, OD, O_2, DO_2 and O_3 (inset) react with Cl_2O, at room temperature, to form the product ions Cl^-, Cl_2^-, $Cl^-(DOCl)$, $ClO^-(DOCl)$, Cl_3O^-, and $Cl_3O_2^-$. Fig. 3 shows the product ion intensity as a function of reactant gas flow, which enables us to infer the reaction sequences. Cl^-, Cl_2^-, $Cl^-(DOCl)$, and $ClO^-(DOCl)$, are the observed product ions arising from the primary $X^-(D_2O)_{n=0-2}/Cl_2O$ encounter. The remaining ion products are formed by subsequent reactions, with $Cl_3O_2^-$ being the most prominent product ion at higher Cl_2O flow.

At lower temperatures where $DO_2^-(D_2O)_4$ and $OD^-(D_2O)_4$ are observed (Fig. 4) product ions are observed (Fig. 5) at masses 124 and 140 amu. These could correspond to the association/switching products $OD^-(D_2O)(Cl_2O)$ and $DO_2^-(D_2O)(Cl_2O)$, respectively. Note that we cannot distinguish these from the possible species $ClO^-(DOCl)(D_2O)$, or $OD^-(DOCl)_2$, and $DO_2^-(DOCl)_2$, respectively.

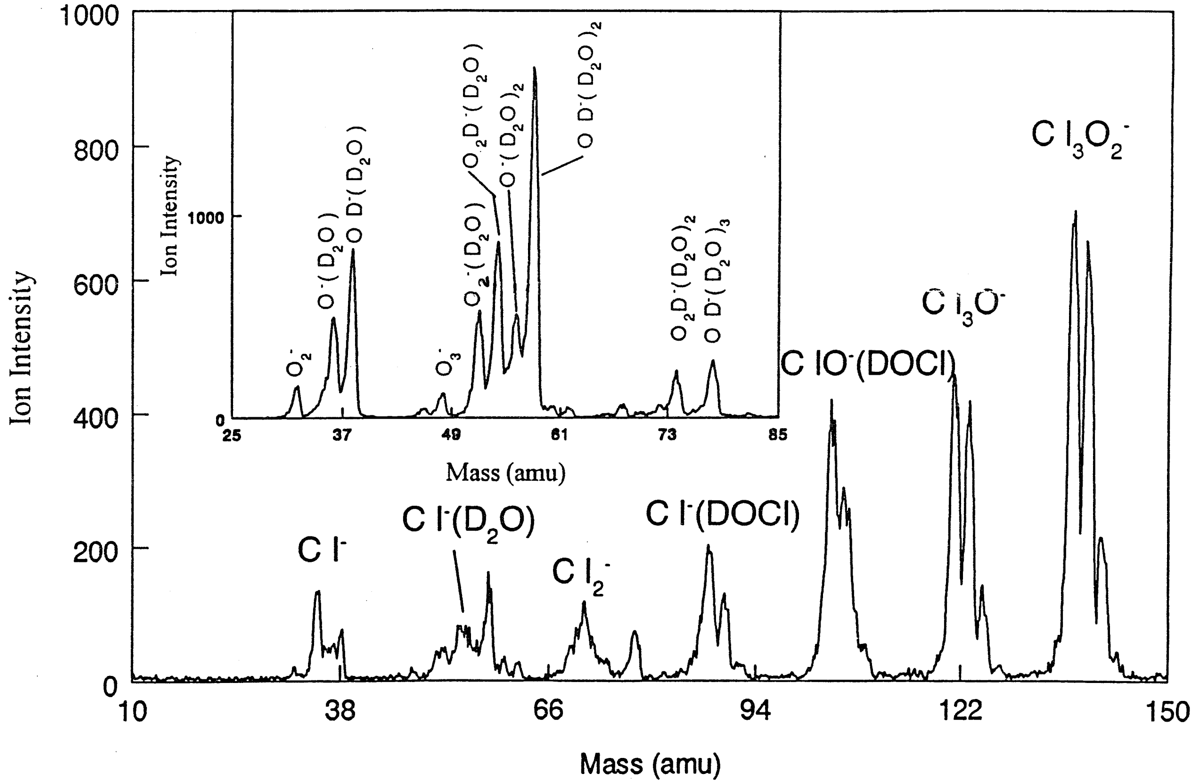


Fig. 1. Mass spectra obtained before (inset) and after addition of 82 sccm of a 0.18% Cl_2O/He mixture through the RGI at room temperature with FT pressure at 0.28 Torr.

Additionally the product ions $Cl_3O_2^-(D_2O)$ and $Cl_3O_2^-(D_2O)_2$ are observed (Fig. 5) at colder temperatures. These ions were not seen in previous studies [7] of NO_2^- $(D_2O)_{n=1,2}$ + Cl_2O reactions, and may be produced from the reaction of Cl_2O with the ions at masses 124 and 140 amu. Further study of these reactions is inhibited by interference of the product ions Cl_3O^- and $Cl_3O_2^-$ at 121 and 137 amu, respectively.

Rate constants were determined for the $X^-(D_2O)_n$ / Cl_2O reactions and are presented in Tables 1–4. The experimental rate constants are compared to the collision rates calculated using the Su–Chesnavich methodology [12]. At room temperature experimental rate constants are close to the calculated collision rates. At colder temperatures, the $O^-(D_2O)_n$ ion family was not as prominent and it was only possible to measure some of the rate constants. Those rate constants that could be measured were observed to decrease with decreasing temperature and were found to be well below the calculated collision rates.

4. Discussion

It is useful at this point to compare the product ions above to those of the $NO_2^-(D_2O)_{n=1-2}$ + Cl_2O reactions [7], which yielded Cl^- $(D_2O)_{n=0-2}$, NO_3^- and Cl_2O^- as the primary product ions, with Cl_3O^- and $Cl_3O_2^-$ as the secondary product ions. The current primary product ions differ from those observed in the above system, because it is not possible to form NO_3^-, and the predominant ion products are Cl^-(DOCl) and ClO^-(DOCl). Although there are no thermodynamic data [13] available for the bond energies D(Cl^-–

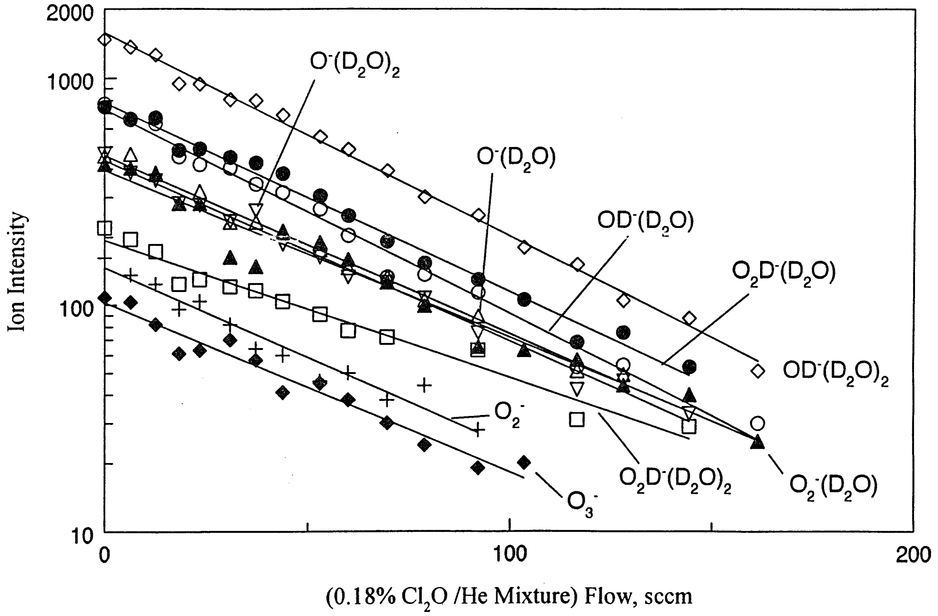


Fig. 2. Observed reactant ion variation recorded for the addition of a 0.18% Cl_2O/He mixture through the RGI at room temperature with FT pressure at 0.28 Torr.

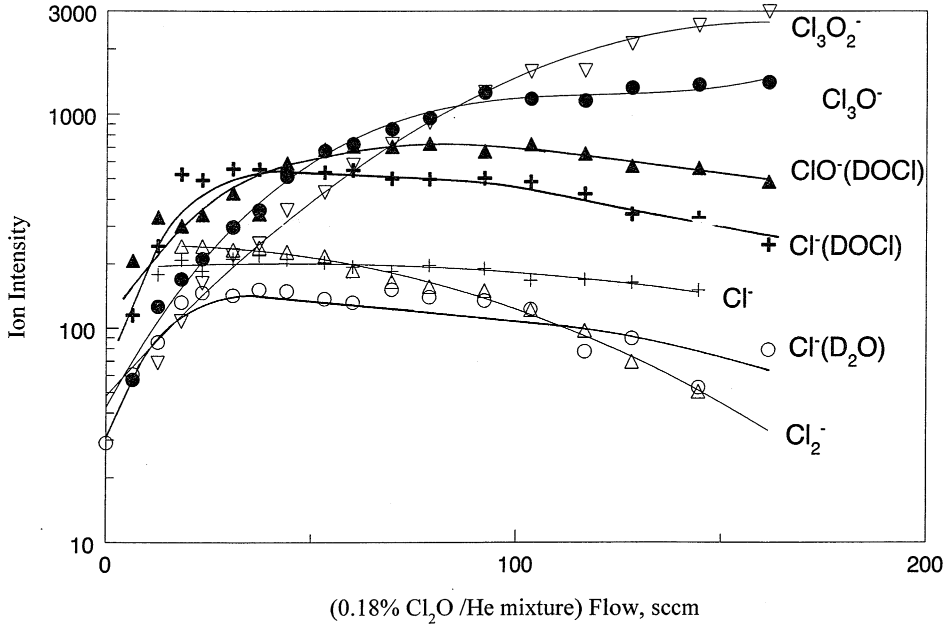


Fig. 3. Observed product ion variation recorded for the addition of a 0.18% Cl_2O/He mixture through the RGI at room temperature with FT pressure at 0.28 Torr.

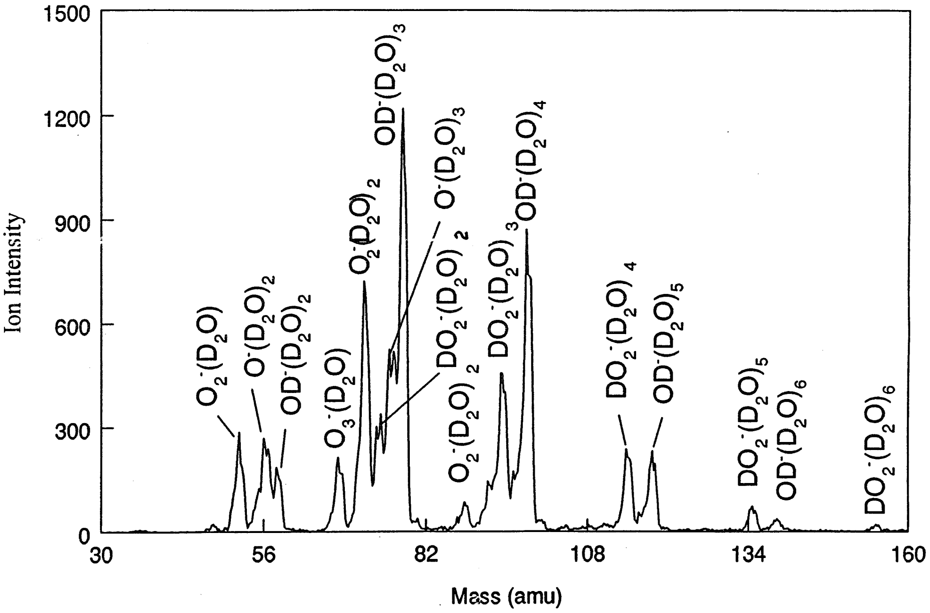


Fig. 4. Mass spectrum obtained before addition of a Cl_2O/He mixture at 170 K with FT pressure at 0.31 Torr.

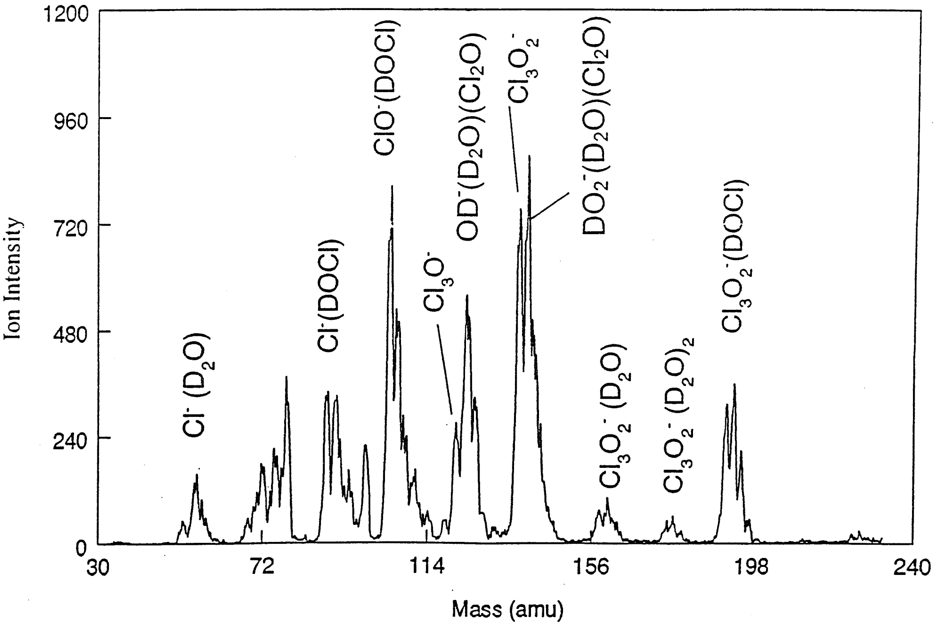


Fig. 5. Mass spectrum obtained after addition of 18.2 sccm of a 0.46% Cl_2O/He mixture through the RGI at 170 K with FT pressure at 0.31 Torr.

Table 1
Rate constants[a] for the reactions of Cl_2O with $O^-(D_2O)_n$ and $OD^-(D_2O)_n$ at indicated temperatures

	$O^-(D_2O)_n$		$OD^-(D_2O)_n$		
n	k_{exp}	k_{cal}[b]	k_{exp}	k_{cal}[b]	T(K)
0	[c]	2.36	2.37 ± 0.28	2.25	184
1	1.42 ± 0.14	1.62	1.33 ± 0.25	1.59	298
2	1.32 ± 0.15	1.40	1.36 ± 0.20	1.39	298
	[c]	1.46	1.51 ± 0.05	1.45	211
	0.98 ± 0.07	1.51	0.96 ± 0.23	1.49	168
3	[c]	1.34	1.38 ± 0.04	1.33	211
	[c]	1.36	1.34 ± 0.07	1.35	184
	[c]	1.37	0.92 ± 0.05	1.37	171
	1.00 ± 0.07	1.58	0.94 ± 0.05	1.37	168
4	[c]	1.28	1.27 ± 0.05	1.28	184
	[c]	1.28	0.90 ± 0.10	1.29	171
	0.99 ± 0.11	1.30	0.91 ± 0.08	1.30	168

[a] Units for all rate constants are: 10^{-9} cm^3 s^{-1}.
[b] Collision rates were determined from the Su–Chesnavich theory [12].
[c] Under these conditions the ion intensity is very small and the rate constants cannot be measured accurately.

DOCl) and D(ClO^-–DOCl), the values are expected to be similar to those of D(Cl^-–DCl) = 23.7 kcal/mol or D(Cl^-–D_2O) = 13.1 kcal/mol. For our analysis in Tables 5–10, we have chosen to use the aforementioned, where a quantitative value is useful in accounting for the present findings. Most of the reaction enthalpies discussed are either highly exothermic or significantly endothermic. The use of the bond energy value 23.7 kcal/mol would not affect the interpretation of our findings. The absence of the products Cl^-(DOCl), and ClO^-(DOCl) in the NO_2^- $(D_2O)_{n=1-2}$ + Cl_2O reaction is easily explained by the thermodynamic analysis in Table 5 which shows both reaction channels are endothermic by 24 and 13 kcal/mol, respectively. The reaction pathway that produces Cl^-(DOCl) would be exothermic if the neutral product was assigned as DNO_3. However, this possibility was not included because it would be more likely to form NO_3^- as the product ion because of its high electron affinity. The results of the NO_2^- $(D_2O)_{n=1-2}$ + Cl_2O system indicate that thermodynamic effects play an important role and that the DOCl observed in the present study is not formed by a neutral / neutral reaction in the flow tube, similar to Reaction (1).

Table 2
Rate constants[a] for the reactions of Cl_2O with $O_2^-(D_2O)_n$ at indicated temperatures

n	k_{exp}	k_{cal}[b]	T(K)
0	1.38 ± 0.11	1.96	298
	1.76 ± 0.12	1.79	184
1	1.29 ± 0.20	1.43	298
	1.51 ± 0.06	1.52	184
	1.31 ± 0.10	1.54	171
	1.30 ± 0.15	1.54	168
2	1.37 ± 0.12	1.48	184
	1.00 ± 0.15	1.49	171
	1.08 ± 0.06	1.49	168
3	1.07 ± 0.06	1.30	184
	0.74 ± 0.09	1.30	168

[a] Units for all constants are 10^{-9} cm^3 s^{-1}.
[b] Collision rates were determined from the Su–Chesnavich theory [12].

Table 3
Rate constants[a] for the reactions of Cl_2O with $DO_2^-(D_2O)_n$ at indicated temperatures

n	k_{exp}	k_{cal}[b]	T(K)
1	1.28 ± 0.18	1.42	298
2	1.16 ± 0.13	1.29	298
	1.45 ± 0.22	1.35	211
	1.00 ± 0.05	1.39	168
3	1.27 ± 0.05	1.29	184
	0.88 ± 0.06	1.31	168
4	1.02 ± 0.08	1.23	184
	0.84 ± 0.09	1.25	168

[a] Units for all rate constants are: 10^{-9} cm^3 s^{-1}.
[b] Collision rates were determined from the Su–Chesnavich theory [12].

Table 4
Rate constants[a] for the reactions of Cl_2O with $O_3^-(D_2O)_n$ at indicated temperatures

n	k_{exp}	k_{cal}[b]	T(K)
0	1.16 ± 0.11	1.47	298
	1.63 ± 0.09	1.56	184
1	1.33 ± 0.12	1.40	184
	1.27 ± 0.09	1.42	171
	1.14 ± 0.15	1.42	168

[a] Units for all rate constants are: 10^{-9} cm^3 s^{-1}.
[b] Collision rates were determined from the Su–Chesnavich theory [12].

Table 5
Enthalpies [13] of reaction for $NO_2^-(D_2O)_n + Cl_2O \rightarrow$ products

$NO_2^-(D_2O)_n + Cl_2O \rightarrow Cl^- + ClONO_2 + n\,D_2O$ (a)

$\rightarrow NO_3^- + Cl_2 + n\,D_2O$ (b)

$\rightarrow Cl^-(DOCl) + NO_2 + OD + (n - 1)\,D_2O$ (c)

$\rightarrow ClO^-(DOCl) + NO_2D + (n - 1)\,D_2O$ (d)

$\rightarrow Cl_2O^- + NO_2 + n\,D_2O$ (e)

Reaction Channel, kcal/mol					
n	a	b	c[a]	d[a]	e
0	−22	−47	[b]	[b]	≤ −5
1	−7	−33	24	13	≤ −19
2	6	−20	11	26	≤ −32

[a] Assume D[Cl⁻–DOCl] = D[ClO⁻–DOCl] = D[Cl⁻–DCl] = 23.7 kcal/mol.
[b] Reaction channel is not possible.

3.1. $O^-(D_2O)_{n=1-4}$

Ab initio calculations [14] have determined that the $O^-(D_2O)$ ion has a structure that is an OD-like dimer rather than an O^-/D_2O complex. Scheme 1 depicts this structure and the role it plays in the $O^-(D_2O)/Cl_2O$ reaction by allowing a hydrogen bonding site near the charge center and extraction of OD or D to form the observed product ions, $Cl^-(DOCl)$ and $ClO^-(DOCl)$. Only the ion products are detected in our experiments, while the neutral products are inferred by mass balance and thermochemical considerations. Table 6 shows the thermochemical analysis of the possible reaction channels of Scheme 1, including the reaction channel (2*f*) producing Cl_2O^-. Most of the reaction channels are highly exothermic, but our experimental results indicate that the reaction channels that form the $Cl^-(DOCl)$ and ClO^- (DOCl) ion products are the most favorable. Products from the highly exothermic reac-

Table 6
Enthalpies [13] of reaction for $O^-(D_2O)_n + Cl_2O \rightarrow$ products

$O^-(D_2O)_n + Cl_2O \rightarrow Cl^- + DOCl + DO_2 + (n - 1)\,D_2O$ (2a)

$\rightarrow Cl^-(D_2O) + ClO_2 + (n - 1)\,D_2O$ (2b)

$\rightarrow Cl_2^- + O_3 + n\,D_2O$ (2c)

$\rightarrow Cl^-(DOCl) + DO_2 + (n - 1)\,D_2O$ (2d)

$\rightarrow ClO^-(DOCl) + OD + (n - 1)\,D_2O$ (2e)

$\rightarrow Cl_2O^- + D_2O_2 + (n - 1)\,D_2O$ (2f)

Reaction Channel, kcal/mol						
n	2a	2b	2c	2d[a]	2e[a]	2f
1	−46	[b]	−100	−110	−74	−29
2	−30	−43	−83	−93	−58	−13
3	−15	−28	−68	−78	−43	3
4	−0.5	−14	−54	−64	−28	17

[a] Assume D[Cl⁻–DOCl] = D[ClO⁻–DOCl] = D[Cl⁻–DCl] = 23.7 kcal/mol.
[b] Reaction channel is not possible.

Table 7
Enthalpies [13] of reaction for $OD^-(D_2O)_n + Cl_2O \rightarrow$ products

$OD^-(D_2O)_n + Cl_2O \rightarrow Cl^- + ClO + OD + n\ D_2O$ (3a)

$\rightarrow Cl^-(D_2O) + ClO + OD + (n - 1)\ D_2O$ (3b)

$\rightarrow Cl_2^- + DO_2 + n\ D_2O$ (3c)

$\rightarrow Cl^-(DOCl) + D_2O_2 + (n - 1)\ D_2O$ (3d)

$\rightarrow ClO^-(DOCl) + n\ D_2O$ (3e)

$\rightarrow Cl_2O^- + DO + n\ D_2O$ (3f)

Reaction Channel, kcal/mol						
n[c]	3a	3b	3c	3d[a]	3e[a]	3f
0	−7	[b]	−39	[b]	−54	−3
1	20	7	−13	−33	−31	20
2	38	24	5	−17	−15	36
3	54	41	21	−2	0.1	51
4	65	60	33	13	14	66

[a] Assume $D[Cl^-–DOCl] = D[ClO^-–DOCl] = D[Cl^-–DCl] = 23.7$ kcal/mol.
[b] Reaction channel is not possible.
[c] Assume $D[O^-(D_2O)_n] = D[OD^-(D_2O)_n] = 22.5, 16.4, 15.1, 14.2, 14.1$ kcal/mol for $n = 1–5$, respectively.

tion channel (2c) are not observed. This supports our interpretation of the species shown in Scheme 1 as a reaction intermediate. The large degree of molecular rearrangement would be too cumbersome for reaction channel (2c) to proceed efficiently.

3.2. $OD^-(D_2O)_{n=1-4}$

The $OD^-(D_2O)_n$ family reacts with Cl_2O in the same manner as the $O^-(D_2O)_n$ family. This is not surprising because of the somewhat similar structures

Table 8
Enthalpies [13] of reaction for $O_2^-(D_2O)_n + Cl_2O \rightarrow$ products

$O_2^-(D_2O)_n + Cl_2O \rightarrow Cl^- + ClO + O_2 + n\ D_2O$ (4a)

$\rightarrow Cl^-(D_2O) + ClO + O_2$ (4b)

$\rightarrow Cl_2^- + O_3 + n\ D_2O$ (4c)

$\rightarrow Cl^-(DOCl) + O_2 + OD + (n - 1)\ D_2O$ (4d)

$\rightarrow ClO^-(DOCl) + DO_2 + (n - 1)\ D_2O$ (4e)

$\rightarrow Cl_2O^- + O_2 + n\ D_2O$ (4f)

Reaction Channel, kcal/mol						
n	4a	4b	4c	4d[a]	4e[a]	4f
0	−39	[b]	−32	[b]	[c]	−48
1	−21	−34	−13	1	3	−30
2	4	−10	4	19	21	−13
3	12	−2	19	35	36	3
4	26	13	34	40	51	17

[a] Assume $D[Cl^-–DOCl] = D[ClO^-–DOCl] = D[Cl^-–DCl] = 23.7$ kcal/mol.
[b] Reaction channel is not possible.

Table 9
Enthalpies [13] of reaction for $DO_2^-(D_2O)_n + Cl_2O \rightarrow$ products

$$O_2D^-(D_2O)_n + Cl_2O \rightarrow Cl^- + DOCl + O_2 + n\,D_2O \tag{5a}$$

$$\rightarrow Cl^-(D_2O) + DOCl + O_2 + (n - 1)\,D_2O \tag{5b}$$

$$\rightarrow Cl_2^- + O_2 + OD + n\,D_2O \tag{5c}$$

$$\rightarrow Cl^-(DOCl) + O_2 + n\,D_2O \tag{5d}$$

$$\rightarrow ClO^-(DOCl) + O + n\,D_2O \tag{5e}$$

$$\rightarrow Cl_2O^- + DO_2 + n\,D_2O \tag{5f}$$

Reaction Channel, kcal/mol

n	5a	5b	5c	5d[a]	5e[a]	5f
0	−70	[b]	−42	−94	−6	−20
1	−52	−65	−24	−75	13	−3
2	−34	−47	−7	−58	30	7
3	−19	−32	9	−43	46	15

[a] Assume D[Cl^-–DOCl] = D[ClO^-–DOCl] = D[Cl^-–DCl] = 23.7 kcal/mol.
[b] Reaction channel is not possible.

involved. Scheme 2 shows the Cl_2O reaction with the OD^- $(D_2O)_2$ ion and how we believe hydrogen bonding at the charge center is important. Thermodynamic analysis of these reaction channels (Table 7) shows that channels (3a) and (3f) (yielding product ions Cl^- and Cl_2O^-, respectively) are exothermic only for $n = 0$, which under most conditions was not observed; Reaction channel (3b) is not possible for $n = 0$. The reaction channels that produce the most prominent primary ion products Cl^-(DOCl) and ClO^-(DOCl) [(3d) and (3e), respectively] are exothermic for certain conditions of hydration as shown in Table 7. Interestingly, at temperatures where $OD^-(D_2O)_4$ is seen (Fig. 4), a product at mass 124 amu is detected (Fig. 5). This could correspond to the association/switching product OD^- $(D_2O)(Cl_2O)$

Table 10
Enthalpies [12] of reaction for $O_3^-(D_2O)_n + Cl_2O \rightarrow$ products

$$O_3^-(D_2O)_n + Cl_2O \rightarrow Cl^- + ClO_2 + O_2 + n\,D_2O \tag{6a}$$

$$\rightarrow Cl^-(D_2O) + ClO_2 + O_2 + (n - 1)\,D_2O \tag{6b}$$

$$\rightarrow Cl_2^- + 2\,O_2 + n\,D_2O \tag{6c}$$

$$\rightarrow Cl^-(DOCl) + O_2 + DO_2 + (n - 1)\,D_2O \tag{6d}$$

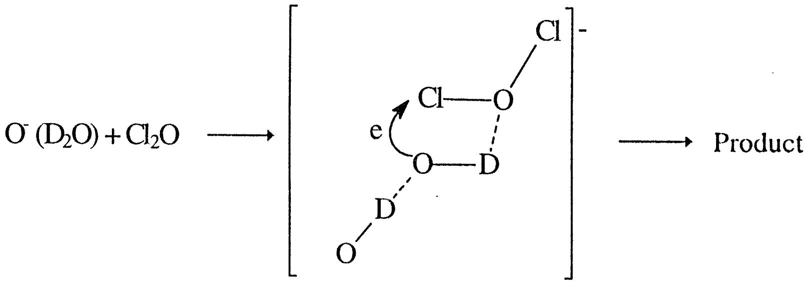
$$\rightarrow ClO^-(DOCl) + O_2 + OD + (n - 1)\,D_2O \tag{6e}$$

$$\rightarrow Cl_2O^- + O_3 + n\,D_2O \tag{6f}$$

Reaction Channel, kcal/mol

n[c]	6a	6b	6c	6d[a]	6e[a]	6f
0	−36	[b]	−60	[b]	[b]	3
1	−18	−31	−24	−22	14	22
2	−0.4	−14	−5	−4	31	39
3	15	2	10	6	47	54

[a] Assume D[Cl^-–DOCl] = D[ClO^-–DOCl] = D[Cl^-–DCl] = 23.7 kcal/mol.
[b] Reaction channel is not possible.
[c] Assume D[$O_3^-(D_2O)_n$] = D[$O_2^-(D_2O)_n$] = 18.4, 17.2, 15.2 kcal/mol.



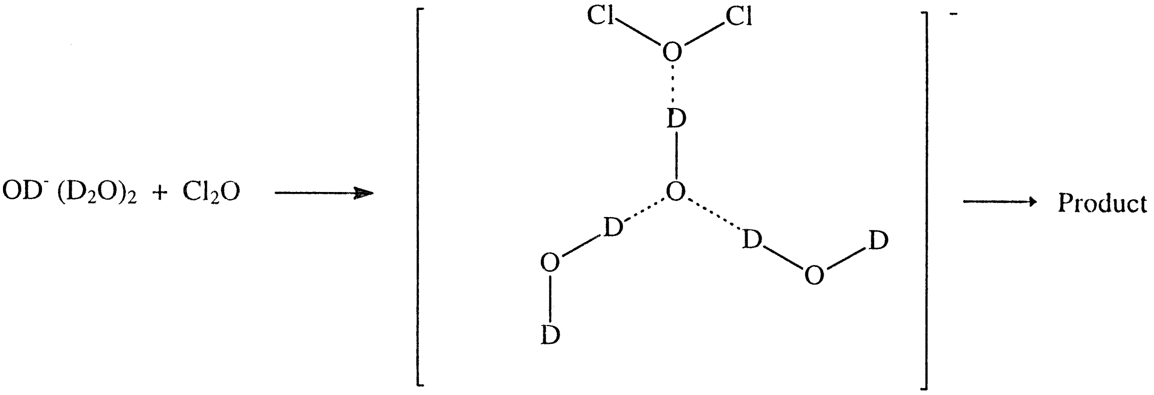
Scheme 1. [See Table 6 for Reactions (2a) through (2e)]

or to reaction channel (3d) with a water attachment, $ClO^-(DOCl)(D_2O)$. However, a more detailed investigation could not be made because of the interference of the isotope pattern of the product ion Cl_3O^- at mass 121 amu.

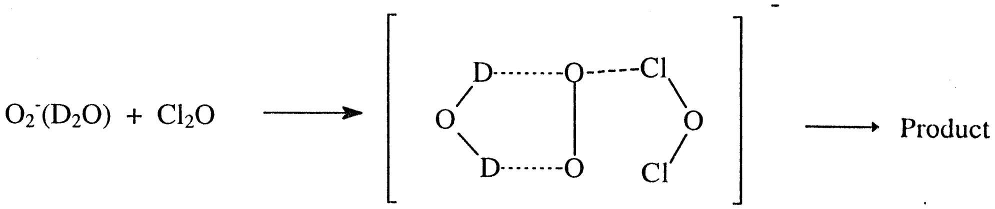
3.3. $O_2^-(D_2O)_{n=0-3}$

In contrast to the two previously discussed ion families, $O_2^-(D_2O)_n$ does not have a site in which Cl_2O can hydrogen bond directly to the charge center. It is more likely that an ion dipole interaction such as is depicted in Scheme 3 represents the reaction intermediate. In order to form the product ions $Cl^-(DOCl)$ and $ClO^-(DOCl)$, either hydrogen bonding to a water ligand with a large distance for the charge transfer or an ion dipole interaction with the charge center, followed by extensive intermolecular rearrangement would be required. Hence, it is unlikely that either mechanism would be operative at or near the collision rate found in the experiments: see Table 2. Further support against formation of the product ions $Cl^-(DOCl)$ and $ClO^-(DOCl)$ from large molecular rearrangement is found in the thermodynamic analysis shown in Table 8. Reaction channels (4d) and (4e) are close to thermoneutral for $n = 1$ and clearly endothermic for $n = 2$ and 3.

Reaction channel (4f), producing Cl_2O^-, is exothermic; however, Cl_2O^- was not observed in the product spectra (Fig. 1) so channel (4f) (Table 8) is not believed to occur. Additionally, the ion intensities of the $O_2^-(D_2O)_n$ family are close to the combined intensities of the product ions Cl^- and Cl_2^-. Thus, if the only two reaction channels used by the $O_2^-(D_2O)_n$/Cl_2O system are (4a) and (4c), these reactions could be the sole contributors to the Cl^- and Cl_2^- product



Scheme 2. [See Table 7 for Reactions (3c) through (3e)]



Scheme 3. [See Table 8 for Reactions (4a) through (4f)]

ions. This conclusion, though intriguing, should be considered speculative and would require a more extensive experimental investigation using the selected ion flow tube (SIFT) technique (which is currently being modified in our laboratory) will be used to further investigate these complex reactions.

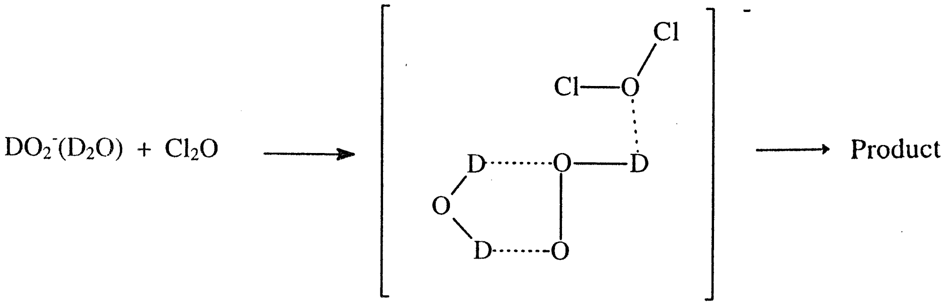
3.4. $DO_2^-(D_2O)_{n=1-4}$

Although the $DO_2^-(D_2O)_n$ family is somewhat similar to the $O_2^-(D_2O)_n$ family in structure, it differs considerably in reactivity. The difference in reactivity is believed to be caused by the ability for Cl_2O to hydrogen bond to the ion center. Scheme 4 depicts this structure and its role in the $DO_2^-(D_2O)_n/Cl_2O$ reaction.

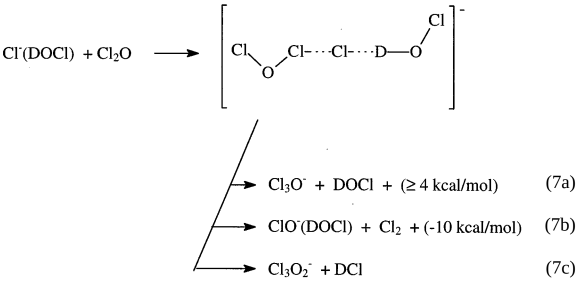
Thermodynamic analysis (Table 9) shows that only Reaction channel (5e) can be excluded for thermodynamic reasons. Reaction channels (5a) and (5b) are possible, but not likely to play an important role because of the relatively low intensity of these ion products in Figs. 1 and 2. Reaction channel (5f) may be excluded because it is barely exothermic for $n = 1$ and the ion product Cl_2O^- was not observed. This leaves Reaction channel (5d) as the main channel for the $DO_2^-(D_2O)_n/Cl_2O$ reaction. This is not surprising because Reaction channel (5d) is the most thermodynamically favored and, most importantly, would require almost no rearrangement to form the $Cl^-(DOCl)$ ion product.

3.5. $O_3^-(D_2O)_{n=0-1}$

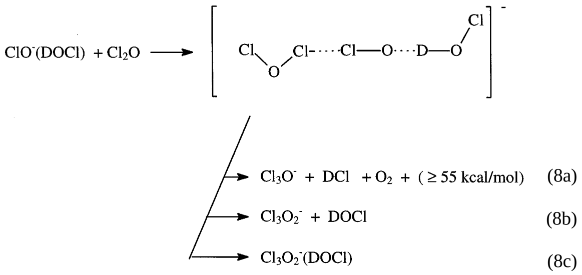
The intensity of the $O_3^-(D_2O)_n$ ion family is small in comparison to the other ion families previously discussed. However, it was possible to determine the rate constants (Table 4) for the $n = 0$ and 1 species. No information is available for the $O_3^-(D_2O)$ structure, so no scheme is presented for this species. The $O_3^-(D_2O)$ structure may be similar to that of the $O^-(D_2O)$ in which partial extraction of a D atom from the water molecule would facilitate the formation of the product ions $Cl^-(DOCl)$ and $ClO^-(DOCl)$. Conversely, the $O_3^-(D_2O)$ structure could be similar to that of $O_2^-(D_2O)$, where the removal of a D atom from a water molecule would have to occur without the assistance of the reactant ion. At this time it can only be speculated that the structure is probably similar to



Scheme 4. [See Table 9 for Reactions (5a) through (5d)]



Scheme 5.



Scheme 6.

that of $O^-(D_2O)$, which would favor the formation of the observation of the ion products $Cl^-(DOCl)$ and $ClO^-(DOCl)$. Because no data were available for either $D[O_3^- – D_2O]$ or $D[O^- – D_2O]$, the thermodynamic analysis in Table 10 used $D[O_2^- – D_2O] = D[O_3^- – D_2O]$. Table 10 shows that Reaction channels (6a)–(6d) are all exothermic for various degrees of hydration, whereas channels (6e) and (6f) are endothermic. Reaction channels (6a)–(6c), though exothermic, are not expected to play a major role in the $O_3^-(D_2O)_n/Cl_2O$ reaction because of the low intensities of their corresponding product ions. However, when $n = 0$, channels (6a) and (6c) are the only options to be considered.

3.6. $Cl^-(DOCl)$

The data in Fig. 3 indicate that the product ion $Cl^-(DOCl)$ undergoes secondary reactions with Cl_2O to form products. This reaction is shown in Scheme 5. The products corresponding to Reaction channels (7a)–(7c) all show some increase in intensity as the $Cl^-(DOCl)$ intensity begins to decrease (Fig. 3). The formation of Cl_3O^- should be facile as a switching reaction, and using the bond energy $D(Cl^- – Cl_2O) \geq 27.8$ kcal/mol determined previously, Reaction channel (7a) is exothermic by ≥ 4 kcal/mol. Reaction channel (7b) is endothermic by 10 kcal/mol and would require significant rearrangement in order to form $ClO^-(DOCl)$. No data are available for ΔH_f^0 $(Cl_3O_2^-)$, but Reaction (7c) would also require rearrangement and is unlikely to occur; on the other hand, it cannot be excluded. However, we believe only Reaction channel (7a) is likely to occur.

3.7. $ClO^-(DOCl)$

Possible secondary reactions of $ClO^-(DOCl)$ with Cl_2O are also observed in Fig. 3. Two ion products are seen to increase in intensity as $ClO^-(DOCl)$ reacts away, namely Cl_3O^-, and $Cl_3O_2^-$. Scheme 6 depicts this reaction with the DOCl molecule intact; it is possible, however, that the $ClO^-(DOCl)$ structure may be more symmetrical with two ClO groups loosely attached to the D atom. This symmetrical structure might have a more delocalized charge and, thus, may react slower than an ion molecule complex such as Cl^- (DOCl). Such an effect would cause the decrease in ion intensity to be more gradual as is seen for the $ClO^-(DOCl)$ species in Fig. 3. We hope that our findings will prompt theoretical interest in performing calculations for these structures in order to determine which is more stable. Reaction channel (8a) is exothermic by at least 55 kcal/mol but would require rearrangement in order to form the proposed neutral products. If DO_2 and Cl instead of DCl and O_2 are used as the neutral products, Reaction channel (8a) would be exothermic by ≥ 1 kcal/mol. Again, there are no thermochemical data available for $Cl_3O_2^-$ as a product ion, but its formation is evident in Figs. 1 and 2. At colder temperatures, Reaction channel (8c) becomes efficient and the association product at mass 190 is observed (Fig. 5).

The reactions of Cl^- $(D_2O)_{n=0–2}$, Cl_2^-, Cl_3O^-, and $Cl_3O_2^-$ with Cl_2O were reported in our previous study of gas phase reactions of Cl_2O with NO_2^- $(D_2O)_{n=0,1,2}$, NO_3^- $(D_2O)_{n=0,1,2}$ and Cl^- $(D_2O)_{n=0–2}$ [7]. These findings are summarized below.

$$Cl^- + Cl_2O \leftrightarrow [Cl_3O^-]^* \rightarrow \text{products} \qquad (9)$$

$$Cl^- (D_2O)_{1,2} + Cl_2O \rightarrow Cl_3O^- + n\, D_2O \qquad (10)$$

$$Cl_2^- + Cl_2O \rightarrow Cl_3O^- + Cl + (\leq 3.6 \text{ kcal/mol}) \qquad (11)$$

Reaction (9) requires collisional stabilization of the $[Cl_3O^-]^*$ species with He; this process is not very efficient as can be determined from Fig. 3, in which the Cl^- intensity remains fairly constant with increasing Cl_2O concentration. The ion product for Reactions (10) and (11) is Cl_3O^-; two other possible ion products, Cl_2O^- and Cl_3^-, were also reported in the earlier study. These products were not observed in the present study and are omitted from further consideration.

$$Cl_3O^- + Cl_2O \rightarrow Cl_3O_2^- + Cl_2 \qquad (12)$$

$$Cl_3O_2^- + Cl_2O \rightarrow Cl_3O_2^-(Cl_2O) \qquad (13)$$

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

There are no thermodynamic data available for the $Cl_3O_2^-$ product ion, but the appearance of the ion at room temperature indicates that Reaction (12) is exothermic. Reactions (13) and (14) occur only at cold temperatures and are presumably termolecular at the flow tube conditions with He acting as the stabilizing gas.

5. Conclusions

This is the first report of the reactions of $X^-(D_2O)_{n=0-4}$ X = O, OD, O_2, DO_2, and O_3, with dichlorine monoxide, Cl_2O. Although Cl_2O is not believed to be directly involved in atmospheric chemistry, current considerations suggest that because of its similarity in structure to species such as the ClO dimer (ClOOCl), which plays an important role in ozone destruction in the polar stratosphere, the ionic reactions presented for this study of Cl_2O may provide information which contributes to a further understanding of the chemistry of atmospherically important chloride compounds (ClO, ClOOCl, HOCl).

Rate constants for the reactions of $X^-(D_2O)_{n=0-4}$ X = O, OD, O_2, DO_2, and O_3 with Cl_2O are close to the calculated collision rate constants at room temperature and decrease as the temperature decreases (within the ranges studied). The predominant primary ion products Cl^- (DOCl) and ClO^- (DOCl) are similar to those expected for the reaction of water with Cl_2O [Neutral Reaction (1)] in which HOCl is the sole product. Thus, ion molecule reactions can accelerate the production of DOCl. The less abundant product ions $Cl^-(D_2O)_{n=0-2}$, and Cl_2^- are also observed in the study [7] of $NO_2^-(D_2O)_{n=0-2}$ charge transfer reactions with Cl_2O. These ion products may also be formed from a charge transfer reaction of one ion family $O_2^-(D_2O)_n$ in which the production of Cl^-(DOCl) and ClO^-(DOCl) is not thermodynamically feasible; see Table 8, Reactions (4d) and (4e). Secondary reactions produce the ion products Cl_3O^- and $Cl_3O_2^-$ at room temperature and $Cl_3O_2^-(D_2O)_{1,2}$ and $Cl_3O_2^-(Cl_2O)_{1,2}$ at lower temperatures.

Acknowledgements

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