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Existence of a Chlorine Oxide and Water ($ClO{\cdot}H_2O$) Radical Complex

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Several mechanisms have been proposed to explain ozone depletion in the Antarctic stratosphere.[1−4] However, most of the catalytic ozone removal processes that have been suggested to date involve ClO. There are two critical steps in these mechanisms: (1) the formation of the ClO dimer and (2) its photodecomposition. The formation of the ClO dimer (reaction 1) requires the presence of a third body to stabilize the dimer; consequently the rates for dimer formation are slow. The question we raise is whether there is a possible chaperone for ClO that could enhance the dimer formation rate. Schaefer and co-workers[5,6] and Nanayakkara[7] et al. noted the existence of a hydroxyl radical−water complex that is bound by 5.6 kcal mol^{-1}. A $ClO{\cdot}H_2O$ radical complex could play a role in enhancing the dimer formation by acting as a chaperone through

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \qquad (1)$$

$$ClO{\cdot}H_2O + ClO \rightarrow Cl_2O_2 + H_2O \qquad (2)$$

In this paper, we use *ab initio* calculations to determine if a $ClO{\cdot}H_2O$ radical complex exists.

The predicted molecular structure[8−11] for the $ClO{\cdot}H_2O$ complex is summarized in Table 1. In the complex, the oxygen of the ClO radical hydrogen bonds to the hydrogen of water, as opposed to the chlorine complexing to the hydrogen. As can be seen from Figure 1, the $ClO{\cdot}H_2O$ radical complex has a skewed nonplanar structure. Structural changes can be seen in the water portion of the complex as a result of the formation of the complex. The HO′ bond length decreases from the length of the HO bond in isolated water calculated at the same level of theory of the complex. Structural results at the higher level of theory show that the complex exhibits stronger hydrogen bonding than at the lower levels. We did explore planar structures on both the $^2A'$ and $^2A''$ potential energy surfaces. We found the planar forms (the configuration in which the terminal chlorine and terminal hydrogen of H_2O are 0° to each other hence is called *cis*, and the other where the angle is 180° hence is called *trans*) to be first-order saddle points. It is interesting to compare the molecular structure of $ClO{\cdot}H_2O$ to the well-characterized $HO{\cdot}H_2O$. Kim et al.[5] have found that the H′·O bond lengths in the $HO{\cdot}H_2O$ complex range from 2.086 to 2.115 Å for the ground state depending on the level of theory. These results suggest that the hydrogen bondings in $ClO{\cdot}H_2O$ and $HO{\cdot}H_2O$ are quite similar, with one notable difference. The O′H′O angle in $HO{\cdot}H_2O$ is close to linear (ranging from 182.0° to 189.8°), while in $ClO{\cdot}H_2O$ it is more bent (ranging from 159.9° to 162.5°). This suggests that the potential energy hypersurface for the O′H′O angle is more flat for $HO{\cdot}H_2O$ than it is for $ClO{\cdot}H_2O$. There are multiple minima for the $ClO{\cdot}H_2O$ complex. Searches for other structures yield a structure with the Cl complexing to the oxygen of H_2O, and a structure in which the Cl complexes to the hydrogen. However, these structures are not lower in energy than the hydrogen-bonded complex given in Table 1 and Figure 1.

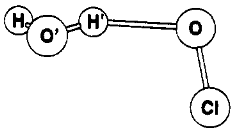

Figure 1. Optimized structure for $ClO{\cdot}H_2O$ radical complex.

The theoretical D_e values for the $ClO{\cdot}H_2O$ complex are given in Table 1. Using the 6-31G(d) basis set we find the predicted D_e to be 3.5 kcal mol^{-1}, and it is little affected by electron correlation. However, extension of the basis set to 6-311G-(2d,2p) increases the predicted D_e to ca. 6.3 kcal mol^{-1}. This is consistent with the observed structural changes, in which we noted that the optimizations with the larger 6-311G(2d,2p) resulted in a structure that is more strongly hydrogen bonded than optimizations with the 6-31G(d) basis set. The dissociation energy for $HO{\cdot}H_2O$ obtained with DZP basis sets is comparable to those we obtained with the 6-31G(d) basis set, namely, $D_e \sim 3.5$ kcal mol^{-1} ($HO{\cdot}H_2O$)[5,6] compared with $D_e \sim 3.5$ kcal mol^{-1} ($ClO{\cdot}H_2O$). Nevertheless, at the highest level of theory, QCISD(T)/6-311G(3df,3pd)//QCISD/6-311G(2d,2p), the D_e is 4.4 kcal mol^{-1} for $ClO{\cdot}H_2O$. Corrections for vibrational zero-point energy yield a value for D_0 of 3.2 kcal mol^{-1}. The estimated uncertainty in the binding energy at our best level of theory is ±2 kcal mol^{-1}. This suggests that the radical complex should be experimentally observable.

In Table 2 are the harmonic vibrational frequencies for $ClO{\cdot}H_2O$ radical complex. Also included are the frequency shifts which are obtained by taking the difference between the vibrational frequencies of the isolated H_2O and ClO molecules and the radical complex using the same basis set at the same level of theory. At the UMP2/6-31G(d) level of theory the HO stretching modes are red shifted; however, the CISD and QCISD frequencies are significantly blue shifted compared with the MP2 frequencies. The bending vibrational frequency of water is predicted to be 1734, 1755, and 1745 cm^{-1} at the UMP2, UCISD, and UQCISD levels of theory, respectively. For the $ClO{\cdot}H_2O$ complex at the same levels of theory the ν_3 mode of the complex is in general upshifted. The ClO stretching mode (ν_4) of the complex is similar to the isolated ClO stretching mode at the ClO radical. At the UMP2/6-31G(d) level, the shift of the ClO stretching modes of the complex is small and to the blue. At the UCISD level it is significantly red shifted by 62 cm^{-1}. At the UQCISD level the shift is 6 cm^{-1} to the blue. There are other modes whose frequencies are well separated from those of the isolated monomers. These are the ν_5 through ν_8 modes. The ν_5 and ν_6 modes, in particular, are predicted to be fairly intense modes. The observation of these modes in a future experiment could support the existence of the $ClO{\cdot}H_2O$ radical complex.

The reaction of ClO radicals with H_2O to produce HOCl and HO radicals is endothermic by 24.7 kcal mol^{-1}. Under atmospheric conditions, this reaction is extremely slow. However, ClO radicals in the presence of water could form the

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Table 1. Optimized Geometries and Dissociation Energies for the $ClO{\cdot}H_2O$ Complex

	geometric parameters[a]								relative energy[b]	
level of theory	r(HO′)	r(H′O′)	r(H′O)	r(ClO)	θ(HO′H′)	θ(O′H′O)	θ(H′OCl)	τ	D_e	D_0
UMP2/6-31G(d)	0.968	0.970	2.138	1.599	104.1	160.3	100.1	125.4	3.5	2.3
UCISD/6-31G(d)	0.961	0.962	2.185	1.612	104.7	162.4	103.5	129.7		
QCISD/6-31G(d)	0.969	0.971	2.164	1.627	104.2	160.7	99.3	130.0	3.6	2.4
UMP2/6-311G(2d,2p)	0.955	0.958	2.087	1.585	103.5	159.9	99.2	126.9	6.3	5.1
UCISD/6-311G(2d,2p)	0.947	0.949	2.158	1.595	104.6	162.5	101.8	136.8		
QCISD/6-311G(2d,2p)	0.957	0.954	2.112	1.616	103.8	162.2	99.5	133.7	4.0	2.8
PMP4/6-311G(2df,2p)									2.9	1.7
UQCISD/6-311G(2df,2p)									4.0	2.8
UQCISD(T)/6-311G(2df,2p)									4.3	3.1
PMP4/6-311G(3df,3pd)									2.9	1.7
UQCISD/6-311G(3df,3pd)									2.9	1.7
UQCISD(T)/6-311G(3df,3pd)									4.4	3.2

[a] Bond distances in angstroms and bond angles in degrees. [b] In kcal mol^{-1}.

Table 2. Harmonic Vibrational Frequencies (cm^{-1}) for the $ClO{\cdot}H_2O$ Complex[a]

		freq (cm^{-1})[b] [shifts (cm^{-1})[c]]		
mode no.	mode description	UMP2	UCISD	UQCISD
1	OH asym str	3906 (106) [14]	4035 (150) [−107]	3905 (134) [15]
2	OH sym str	3770 (47) [8]	3922 (37) [−114]	3790 (36) [−18]
3	HOH bend	1742 (78) [−8]	1811 (84) [−56]	1791 (73) [−36]
4	ClO str	852 (33) [3]	888 (13) [−62]	849 (7) [6]
5	O−H′···O bend	395 (181)	654 (222)	675 (209)
6	HOH′ rock	206 (108)	575 (100)	617 (148)
7	HO(H_2O) out of plane bend	151 (6)	520 (135)	575 (101)
8	H′···O str	70 (119)	262 (7)	262 (7)
9	H′···OCl bend	42 (34)	94 (1)	101 (1)

[a] All frequencies for the various levels of theory are calculated with the 6-31G(d) basis set. [b] Intensity given in parentheses in km mol^{-1}. [c] Shifts are relative to the monomer frequencies in H_2O and ClO.

$ClO{\cdot}H_2O$ complex. Using an estimate of the entropy for the $ClO{\cdot}H_2O$ complex (71 cal mol^{-1} K^{-1}), and using the $ClO{\cdot}H_2O$ binding energy, we can calculate a range for the estimated equilibrium constant at 200 K (the average temperature in the region of polar stratospheric clouds) of $2.3 \times 10^{-22} < K_{eq}(200) < 1.5 \times 10^{-19}$. (It should be noted that the equilibrium constant for $ClO{\cdot}H_2O$ is quite similar to that for the reactions $Cl + CO \leftrightarrow ClCO$ and $Cl + O_2 \leftrightarrow ClOO$.[12]) Using K_{eq} we can calculate a specific enhancement of the rate of formation for ClO dimer by reaction 2 over that of reaction 1 by

$$\epsilon = k_b K_{eq}/k_t \tag{3}$$

where k_t is the three-body rate for ClO dimer formation and k_b is the bimolecular rate and K_{eq} is the equilibrium constant for formation of the $ClO{\cdot}H_2O$ complex. If we assume that the rate for $ClO{\cdot}H_2O$ + ClO is gas-kinetic and the three-body rate constant is $\sim 10^{-32}$ cm^6 molecule^{-2} s^{-1}, then a specific enhancement of the rate (ϵ) can be between 2 and 2000. The enhancement can be lower assuming there is an activation barrier associated with the $ClO{\cdot}H_2O$ + ClO process. Nevertheless, this estimate suggests that the significance in the rate enhancements could be dramatic. This particularly applies to conditions under high water vapor pressures and low temperatures.

Water vapor has been experimentally shown to impact the rate of the three-body recombination rate for the $HO_2 + HO_2$ reaction. Lii et al.[13] observed the dependence of the rate constant on water vapor pressure and suggested that the dependence in the rate constant depends on a multistep mechanism that assumes a rapid equilibrium to exist in the formation of a water-complexed HO_2, viz.

$$HO_2 + H_2O \leftrightarrow HO_2{\cdot}H_2O \tag{4}$$

$$HO_2 + HO_2{\cdot}H_2O \rightarrow HO_2 + O_2 + H_2O \tag{5}$$

Kircher and Sander[14] re-examined the experiments of Lii et al.[13] and found that the effect of water vapor on the reaction rate has a strong temperature dependence. In fact the rate was found to be enhanced by as much as a factor of 3. Such an experimental observation for the $HO_2 + HO_2$ case lends credibility to the experimental possibility for a chaperone mechanism for ClO operating at low temperatures in a high water vapor environment. More recently, Morokuma and Muguruma[15] and Kolb et al.[16] have made a similar finding for $SO_3{\cdot}H_2O$ complexes.

In regions where the water concentrations are low, it seems unlikely that such processes could have a significant impact. For example, in the stratosphere around 25 km, the H_2O concentration is on the order of 10^{13} molecule cm^{-3}, and the $[ClO{\cdot}H_2O]/[ClO]$ ratios are too small for this to be a significant mechanism to enhance dimer formation through the complex even though the rate enhancement may be favorable. However, where these species could play a role in the atmosphere is in the marine boundary layer. In this region the water density[17] is on the order of 10^{16} molecule cm^{-3}, the mean temperature[17] is 245 K, and the ClO density[18] is on the order of 10^6 molecules cm^{-3}. This implies that on average 10^2 $ClO{\cdot}H_2O$ clusters should exist in a column of 10^6 ClO molecules. If the specific rate enhancement, ϵ, is on the order of 10^3, then the chaperone mechanism could be an additional and competitive channel for dimer formation.

The intriguing finding of this work is that theory predicts the existence of a $ClO{\cdot}H_2O$ complex that is bound. The complex can act to alter expected three-body reaction kinetics. Our work further suggests the possibility that radical/water clusters could have kinetic roles in the atmosphere, particularly in regions that have high water content and low temperatures characteristic of the polar marine boundary layer.

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