Quantum Mechanical Studies for Proton Transfer in HOCl + HCl and H$_2$O + ClONO$_2$ on Water Clusters

Yongho Kim,*　Chea-Yong Park, and Kyung Hyun Kim

*Department of Chemistry, Kyung Hee University, Yongin 449-701, Korea. *E-mail: yhkim@khu.ac.kr*
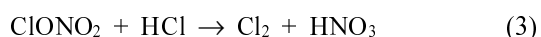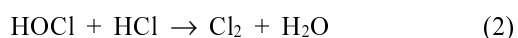*Received October 2, 2005*

We have performed high-level quantum mechanical calculation for multiple proton transfer in HOCl + HCl and H$_2$O + ClONO$_2$ on water clusters, which can be used as a model of the reactions on ice surface in stratospheric clouds. Multiple proton transfer on ice surface plays crucial role in these reactions. The structures of the clusters with 0-3 water molecules and the transition state structures for the multiple proton transfer have been calculated. The energies and barrier heights of the proton transfer were calculated at various levels of theory including multi-coefficient correlated quantum mechanical methods (MCCM) that have recently been developed. The transition state structures and the predicted reaction mechanism depend very much on the level of theory. In particular, the HF level can not correctly predict the TS structure and barrier heights, so the electron correlation should be considered appropriately.

Key Words : Multiple proton transfer, Water cluster, HOCl and ClONO$_2$, Asynchronous transition state

Introduction

The production of photolyzable chlorine (Cl$_2$) from chlorine nitrate (ClONO$_2$) and hydrochloric acid (HCl) is an efficient heterogeneous process in stratospheric cloud that influences ozone depletion in the Antarctic stratosphere.[1-12] Halogen atoms are stored in almost inert reservoir species (ClONO$_2$, HCl, and HBr) and released into more active forms through several reactions mainly on ice particle in polar stratospheric clouds (PSC). One of the main reactions is the hydrolysis of ClONO$_2$ that produces HOCl. There are two common ways of how HOCl can react further on. First, in the presence of HCl or HBr, it is very likely that HOCl reacts with one of these molecules. Secondly, if HOCl is desorbed from the PSC it will be quickly photolyzed to form reactive species like the HO and Cl radicals.

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (1)$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O \qquad (2)$$

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \qquad (3)$$

Reactions (1) and (2) are crucial steps for the final release of reactive halogen species, which are known to occur mainly heterogeneously in the stratosphere whereas the homogeneous gas-phase reactions are considered to be more or less unimportant. Hanson[13] has established the Cl-ONO$_2$ bond cleavage on pure H$_2$^{18}O ice, and Sodeau, *et al.*[14] have proposed that reaction (1) occurs *via* the two step mechanism with the nucleophilic attack of a neutral water molecule on Cl, on the basis of IR bands assigned to the reactive intermediate H$_2$OCl$^+$ ion. Later, Hynes and coworkers[15,16] reported that a water molecule is not likely to be a strong nucleophile to cleave the Cl-ONO$_2$ bond, even taking into account solvation effects, and H$_2$OCl$^+$ ion is not likely to be present on ice surface. They found that the attacking water becomes an OH$^-$-like moiety, a nucleophile much stronger

than H$_2$O, by transferring a proton to the ice lattice from quantum chemical reaction path calculations. They also found that the H$_2$OCl$^+$NO$_3^-$ ion pair proposed by Sodeau *et al.* was not identifiable along the calculated reaction path.

Because of the great importance of these reactions, there are not only experimental but also several theoretical studies on the reaction of HOCl with HCl.[17-20] Apart from studies investigating the reaction there are also studies on the interactions of HCl, and HOCl with water/ice-clusters, respectively. Many theoretical studies have concentrated on the influence of water molecules on the reaction barrier[18,20] and an anion on the reaction barrier.[19] Xu has investigated the reaction of HOCl with HCl in water clusters with ab initio methods.[18] They reported that the reaction barrier is lowered systematically by adding water molecules in the reaction. Without water the reaction barrier is 55.3 kcal/mol, whereas for the water catalyzed reactions it lowers to 48.1 kcal/mol, 16.1 kcal/mol, and 14.4 kcal/mol with one, two, and three water molecules, respectively, at the MP2//HF/6-31G(d) level of theory. They have also showed that inclusion of so-called structural or spectator water molecules lowers the barrier significantly down to an almost barrierless situation. Xu and Zhao have also investigated the reaction of ClONO$_2$ with H$_2$O in water clusters with ab initio methods.[21] Recently Liedl and coworkers have calculated reaction rates for the conversion of HOCl by HCl into Cl$_2$, supported by *n* = 0, 1, 2, and 3 water molecules, using variational transition state theory including tunneling corrections.[22] They have reported an H$_2$OCl$^+$Cl$^-$-like complex at the transition state of HOCl + HCl.

Most of theoretical studies about these reactions on ice or water clusters were based on either density functional theory[22] or Hartree-Fock (HF) levels of theory, although some Post-HF levels of studies are available using the electronic structure obtained at the HF level.[15,16,18,21] Obviously higher level of electronic structure theory should be applied

systematically to understand the mechanism of these important reactions. In this study we have performed systematic post-HF theory calculations including recently developed multi-coefficient correlated quantum mechanical methods (MCCM). We have calculated reactants, products, and transition states for these reactions with n = 0, 1, 2, and 3 water molecules to model these reactions on ice.

Computational Methods

Electronic structure calculations at the HF and MP2 levels were done using the GAUSSIAN 98 quantum mechanical packages.[23] Geometries for hydrated complexes of HOCl and $ClONO_2$ with n = 0, 1, 2, and 3 water molecules were optimized initially at the Hartree-Fock (HF) level of theory using the 6-31G(d,p) basis set, and these structures were used to obtain MP2/6-31G(d,p) structures. The structures for transition states and products for the proton transfer reactions were also calculated. Frequencies were calculated at the MP2 level and scaled by 0.9676 for the zero-point energies.

All of the multi-coefficient correlated quantum mechanical methods (MCCMs) have been described elsewhere in detail;[24-28] therefore, only a short description of each method employed will be given here. Since all of these methods involve differences between energies at different basis sets and theory levels, a short notation has been used in order to write the equation for a multilevel energy succinctly. In this notation, the pipe "|" is used to represent the energy difference either between two one-electron basis sets B1 and B2 or between two levels of electronic structure theory L1 and L2, *e.g.*, Møller–Plesset second-order perturbation theory and Hartree–Fock theory. The energy difference between two basis sets is represented as

$$\Delta E(L/B2|B1) = E(L/B2) - E(L/B1) \qquad (1)$$

where L is a particular electronic structure method, and B1 is smaller than B2. The energy change that occurs upon improving the treatment of the correlation energy is represented by

$$\Delta E(L2|L1/B) = E(L2/B) - E(L1/B) \qquad (2)$$

where L1 is a lower level of theory than L2, and B is a common one-electron basis set. Finally, the change in energy increment due to increasing the level of the treatment of the correlation energy with one basis set as compared to the increment obtained with a smaller basis set is represented as

$$\Delta E(L2|L1/B2|B1) = \\ E(L2/B2) - E(L1/B2) - [E(L2/B1) - E(L1/B1)] \qquad (3)$$

The Utah variant of MCCM (MCCM-UT-CCSD) methods are written as

$$E(\text{MCCM-UT-CCSD}) = \\ c_1 E(\text{HF/cc-pVDZ}) + c_2 \Delta E(\text{HF/cc-pVTZ|cc-pVDZ}) \\ + c_3 \Delta E(\text{MP2|HF/cc-pVDZ}) \\ + c_4 \Delta E(\text{MP2|HF/cc-pVTZ|cc-pVDZ})$$

$$+ c_5 \Delta E(\text{CCSD|MP2/cc-pVDZ}) + E_{SO} + E_{CC} \qquad (4).$$

The MCCM method assigns coefficients to each energy difference involved in the linear combination; the coefficients have been optimized to fit the atomization energies of 82 molecules containing first-and-second-row elements.[29] The basis set deficiency has been corrected by the linear combination of the energy difference with optimized coefficients.

The multilevel structure, energy, and Hessian are calculated by using the MULTILEVEL 3.1 program.[30] This program uses the GAUSSIAN 98 package[23] to obtain the energy, gradient, and Hessian components and then combines the components to calculate the multilevel energy, gradient, and Hessian. Single-level Hessians were used with the Newton–Raphson step. In most cases, an HF/6-31G(d,p) Hessian was recalculated every three steps, and this matrix was used in the determination of every Newton–Raphson step for all MULTILEVEL optimizations. The molecules have been optimized to a structure that has a maximum gradient component less than 1.0×10^{-4} atomic unit. For the structure optimization of HOCl + HCl complexes at the MCCM-UT-CCSD level, the convergence criterion was increased to 6.0×10^{-4} atomic unit.

Results and Discussion

HOCl + HCl → H_2O + Cl_2 (HW0). The geometrical
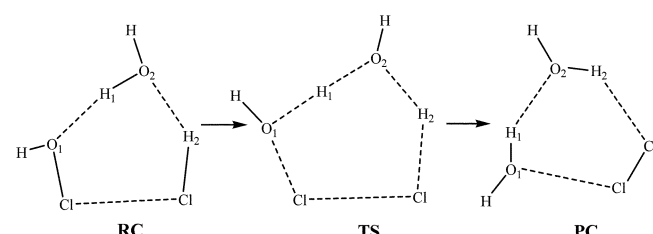
Table 1. Geometric parameters for RC, TS, PC in HOCl + HCl → Cl_2 + H_2O (HW0)

	r_{O-Cl}	r_{O-H}	r_{H-Cl}	r_{Cl-Cl}
		RC		
HF/6-31G(d)[a]	1.669	2.140	1.270	
HF/cc-pVDZ	1.679	2.150	1.282	4.560
B3LYP/6-31+G(d)	1.726	1.943	1.303	4.333
MP2/6-31G(d,p)	1.717	1.978	1.279	4.178
MCCM-UT-CCSD	1.697	2.027	1.281	4.143
		TS		
HF/6-31G(d)[a]	2.087	0.969	2.111	2.717
HF/cc-pVDZ	2.084	0.973	2.037	2.706
B3LYP/6-31+G(d)	2.162	1.011	1.975	2.886
MP2/6-31G(d,p)	2.100	0.982	1.798	2.818
MCCM-UT-CCSD	2.054	1.028	1.798	2.667
		PC		
HF/6-31G(d)[a]		0.947	3.363	1.991
HF/cc-pVDZ	2.869	0.947	5.340	2.013
MP2/6-31G(d,p)	2.734	0.963	5.035	2.028
MCCM-UT-CCSD	2.828	0.960	5.217	2.007

[a]Ref. 18.

parameters for reactant complex (RC), transition state (TS), and product complex (PC) calculated at various levels of theory are listed in Table 1. The geometries from the MCCM and MP2/6-31G(d,p) methods agree well with each other. At RC a hydrogen bond is formed between HCl and the oxygen of HOCl. Its bond length is about 1.9-2.2 Å depending on the computational level, and its bond energies at the MP2/6-31G(d,p) level are 3.5 and 5.1 kcal/mol with and without zero-point energy correction, respectively. At the TS, this hydrogen bond becomes quite short (~1.0 Å), which is comparable to a normal O-H bond distance. When the reaction goes from RC to TS, the MCCM and the MP2/6-31G(d,p) levels of theory predict that the O-Cl bond length of HOCl is increased from 1.7 to 2.1 Å, and the H-Cl bond length is increased from 1.3 to 1.8 Å. One can see that an H_2O moiety is formed at the TS, however it doesn't seem to be a part of $[H_2OCl]^+$ since the O-Cl bond distance is partly

broken (about 0.4 Å larger than a normal O-Cl bond) and the Cl-Cl bond is partly formed (about 0.7 Å larger than a normal Cl-Cl bond).

HOCl + HCl + H_2O → $2H_2O$ + Cl_2 (HW1). The geometrical parameters for RC, TS, and PC computed at various levels of theory are listed in Table 2. No intermediate is found at the computation levels in this study, which means that this reaction occurs in a concerted mechanism. The TS structures optimized at the HF and B3LYP levels are quite different from the MP2 and MCCM structures. The O1-H1 and O2-H1 distances of TS are 1.05 and 1.46 Å, respectively, at the HF/6-31G(d) level, and 1.03 and 1.55 Å, respectively, at the B3LYP/6-31+G(d) level. The O1-Cl distances at the TS are only about 0.1 Å larger than those of RC, and the O2-H2 and H2-Cl distances are very short and long, respectively, which indicates that the transition state is very early in terms of the O1-Cl bond cleavage and late in terms of two proton (H1 and H2) transfer. These results imply the formation of an $[H_2OCl]^+Cl^-$-like complex at the TS, which is consistent with previous study.[22] However the geometries from the MP2 and MCCM levels are quite different. For instance, the O1-H1 and O2-H1 distances are 1.50 and 1.07 Å, respectively, at the MP2/6-31+G(d,p) level, and 1.53 and 1.06 Å, respectively, at the MCCM-UT-CCSD level. The O1-Cl distance is increased by about 0.2 Å, whereas the H2-Cl distance is increased by about 0.7 Å going from RC to TS. The transition state is very early in terms of the H1 transfer but late in terms of the H2 transfer, which suggests that instead of forming an $[H_2OCl]^+Cl^-$-like complex the $H_3O^+Cl^-$-like complex is actually formed at the TS. The partial charges from the Mulliken population analysis at the MP2/6-31G(d,p) level are +0.74 and -0.65 for the H_3O^+ and Cl^- moieties, respectively. Previous studies using the HF level of theory for geometry optimization,[22] could lead inaccurate prediction for the transition state.

HOCl + HCl + $2H_2O$ → $3H_2O$ + Cl_2 (HW2). The geometrical parameters of the HOCl + HCl complex with two water molecules are listed in Table 3. The hydrogen bond distances in RC and PC predicted by the MP2 and B3LYP levels are slightly shorter than those from the HF level. No intermediate is found in this reaction too. At the HF/6-31G(d) level, the O1-H1 and O2-H1 distances at the TS is 1.381 and 1.069 Å, respectively, which means that no $[H_2OCl]^+$-like moiety is formed in this reaction. The O2-H2, O3-H2, and O3-H4 distances are 1.013, 1.557, and 0.967 Å, respectively. The transition state predicted at the HF level is very early in terms of the H1 transfer and very late in terms of the H2 and H4 transfers, which suggests that $[H_3O]^+[H_2O]Cl^-$-like moiety is formed at the TS. However the MP2 level predicts quite different transition state structure, *i.e.*, the O2-H1, O2-H2, O3-H2, and O3-H4 distances are 1.032, 1.225, 1.187, and 1.020 Å, respectively. The transition state is early and late in terms of the H1 and H4 transfers, which is consistent with the HF result. The main difference is in the location of H2 atom at the TS. The H2 atom is in between two oxygen atoms, O3 and O2,

Table 2. Geometric parameters for RC, TS, PC in HOCl + H_2O + HCl → Cl_2 + $2H_2O$ (HW1)

	r_{O1-H1}	r_{H1-O2}	r_{O2-H2}	r_{H2-Cl}	r_{Cl-Cl}	r_{Cl-O1}
RC						
HF/6-31G(d)[a]	2.072		1.924			
HF/cc-pVDZ	2.207		1.911		4.499	
B3LYP/6-31+G(d)	1.994		1.718		4.455	
MP2/6-31G(d,p)	2.024		1.753		4.113	
MP2/6-31+G(d,p)	2.032		1.834		4.355	
MP2/cc-pVTZ	2.024		1.714		3.960	
MP2/tz2p	2.030		1.758		4.065	
MCCM-UT-CCSD	2.074		1.790		3.957	
TS						
HF/6-31G(d)	1.054	1.455	0.979	2.261	2.851	1.769
HF/cc-pVDZ	1.100	1.341	0.982	2.233	2.773	1.788
B3LYP/6-31+G(d)	1.034	1.553	0.989	2.208	2.936	2.103
MP2/6-31G(d,p)	1.461	1.086	1.032	2.021	2.552	1.937
MP2/6-31+G(d,p)	1.503	1.070	1.039	1.975	2.527	1.957
MP2/cc-pVTZ	1.568	1.058	1.047	1.951	2.427	1.925
MP2/tz2p	1.619	1.046	1.044	1.948	2.439	1.970
MCCM-UT-CCSD	1.531	1.062	1.032	2.025	2.413	1.906
PC						
HF/6-31G(d)[a]		1.982		4.917		
HF/cc-pVDZ		1.996		5.200		2.799
MP2/6-31G(d,p)		1.897		4.148		2.629
MP2/6-31+G(d,p)		1.897		5.619		2.672
MP2/cc-pVTZ		1.898		4.003		2.678
MP2/tz2p		1.907		3.989		2.654
MCCM-UT-CCSD		1.930		4.058		2.750

[a]Ref. 18

Table 3. Geometric parameters for RC, TS, PC in HOCl + 2H₂O + HCl → Cl₂ + 3H₂O (HW2)

	$r_{O1\text{-}H1}$	$r_{H1\text{-}O2}$	$r_{O2\text{-}H2}$	$r_{H2\text{-}O3}$	$r_{O3\text{-}H4}$	$r_{H4\text{-}Cl}$	$r_{Cl\text{-}Cl}$	$r_{Cl\text{-}O1}$
				RC				
HF/6-31G(d)[a]	2.056		1.918		1.867			
HF/cc-pVDZ	2.081		1.931		1.875		3.801	
B3LYP/6-31+G(d)	1.925		1.799		1.667		3.157	
MP2/6-31G(d,p)	1.951		1.821		1.708		3.288	
				TS				
HF/6-31G(d)[a]	1.381	1.069	1.013	1.557	0.967	2.285	2.493	1.811
HF/cc-pVDZ	1.446	1.034	1.026	1.480	0.971	2.197	2.507	1.811
B3LYP/6-31+G(d)	1.542	1.039	1.258	1.183	1.036	1.925	2.486	1.919
MP2/6-31G(d,p)	1.523	1.032	1.225	1.187	1.020	1.922	2.477	1.892
				PC				
HF/6-31G(d)[a]		2.009		2.028		3.382		
HF/cc-pVDZ		1.967		1.954		4.230		2.860
MP2/6-31G(d,p)		1.792		1.848		2.916		2.505

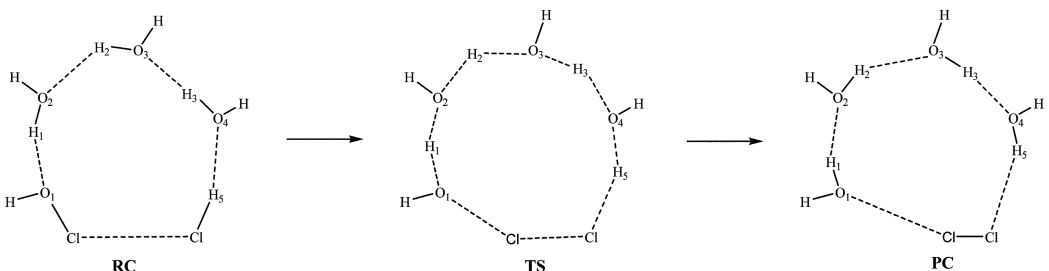[a]Ref. 18

although slightly closer to the O3 atom, which indicates that the H₅O₂⁺-like complex is formed at the TS. The H₅O₂⁺ complex an important form of protonated water clusters.[31-33] Once a proton is almost completely transferred from HCl to a neighboring water molecule, then this molecule in turn generates probably a short and strong hydrogen bond to the second water molecule to form a H₅O₂⁺-like complex. These results imply that the [H₅O₂]⁺Cl⁻-like moiety is formed at the MP2 level. The TS structure from the B3LYP method agrees well with the MP2 structure.

HOCl + HCl + 3H₂O → 4H₂O + Cl₂ (HW3). Xu[18] and Voegele *et al.*[22] have calculated the HOCl + HCl complex with three water molecules and predicted the transition state for this reaction involving three water molecules with quadruple proton transfer. They suggest that the reaction mechanism of this complex seem very similar to the mechanism occurring on a hexagonal ice surface. They have also reported that the barrier height of this reaction is lowered greatly compared to those with two or fewer water molecules. The geometrical parameters of RC, PC, and TS are listed in Table 4. The geometries reported by Xu[18] and Voegele *et al.*[22] have also listed. The HF level predicts the [H₃O]⁺-like moiety is formed in the TS adjacent to HOCl, and all protons are almost transferred to the acceptor atoms. This may suggest that the reaction mechanism is similar to the above mechanism where the HCl proton is transferred to the first water molecule, which shuttles its hydrogen-bonded proton to the next water molecule and so forth. However at the MP2 level, no [H₃O]⁺-like moiety is present at TS and

most protons in water molecules are not transferred yet except for the first water molecule adjacent to HCl. The bond distances for O3-H3 and O4-H3 at TS are 1.248 and 1.168 Å, respectively, and the O4-H5 bond length is 1.046 Å. This result implies that the HCl proton is transferred to the first water molecule, which shuttles its proton toward the second water molecule. However the proton in the second water molecule hardly moves toward the third water molecules, which suggests the possibility of an intermediate. We have calculated an intermediate at the MP2 level as shown in Figure 1. In intermediate, an [H₃O]⁺-like moiety appears at the center of three bridging water molecule, and a Cl⁻-like species is formed and doubly hydrogen bonded with H₃O⁺ and H₂O. The partial charge on this Cl from the Mulliken population analysis is −0.71. The TS is not for the concerted quadruple proton transfer but for the stepwise reaction from RC to an intermediate. The second TS between the intermediate and PC is not calculated. The energy of the intermediate is about 1.9 kcal/mol lower than that of the TS. These results suggest that the reaction on a ice surface would occur stepwise and an [H₃O]⁺- and a Cl⁻-like species could be formed.

An accurate prediction for the energetics is important to understand the mechanism of these reactions. The HF level of theory and the density functional theory overestimates and underestimates the barrier heights, respectively, in general. A newly developed multicoefficient correlated quantum mechanical method (MCCM) has been used to predict energetics of various reactions very accurately with

Table 4. Geometric parameters for RC, TS, PC in $HOCl + 3H_2O + HCl \rightarrow Cl_2 + 4H_2O$ (HW3)

	$r_{O1\text{-}H1}$	$r_{H1\text{-}O2}$	$r_{O2\text{-}H2}$	$r_{H2\text{-}O3}$	$r_{O3\text{-}H3}$	$r_{H3\text{-}O4}$	$r_{O4\text{-}H5}$	$r_{H5\text{-}Cl}$	$r_{Cl\text{-}Cl}$	$r_{Cl\text{-}O1}$
					RC					
HF/6-31G(d)[a]	2.080	0.952	1.918	0.957	1.899	0.959	1.810	1.291		1.673
HF/cc-pVDZ	2.048	0.951	1.919	0.956	1.882	0.958	1.829	1.302	3.642	1.683
B3LYP/6-31+G(d)[b]	1.846	0.982	1.770	0.989	1.718	0.966	1.566	1.367	2.935	1.758
MPW1K/6-31+G(d,p)[b]	1.883	0.963	1.781	0.971	1.692	0.979	1.542	1.346	3.024	1.695
MP2/6-31G(d,p)	1.892	0.971	1.794	0.978	1.738	0.984	1.630	1.323	3.129	1.728
					TS					
HF/6-31G(d)[a]	1.435	1.038	1.030	1.468	0.976	1.704	0.964	2.231	2.542	1.785
HF/cc-pVDZ	1.530	1.001	1.109	1.282	0.989	1.597	0.971	2.115	2.597	1.771
B3LYP/6-31+G(d)[b]	1.548	1.027	1.405	1.079	1.117	1.333	1.019	1.943	2.480	1.917
MPW1K/6-31+G(d,p)[b]	1.829	0.969	1.629	0.989	1.225	1.166	1.028	1.843	2.721	1.734
MP2/6-31G(d,p)	1.872	0.975	1.669	0.995	1.248	1.168	1.046	1.820	2.835	1.759
					PC					
HF/6-31G(d)[a]	0.960	1.875	0.959	1.889	0.958	1.910	0.962	3.377	1.995	
HF/cc-pVDZ	0.956	1.910	0.956	1.899	0.955	1.941	0.948	2.878	2.023	2.693
MP2/6-31G(d,p)	0.984	1.743	0.981	1.765	0.976	1.822	0.965	2.494	2.068	2.435

[a]Ref. 18. [b]Ref. 22.
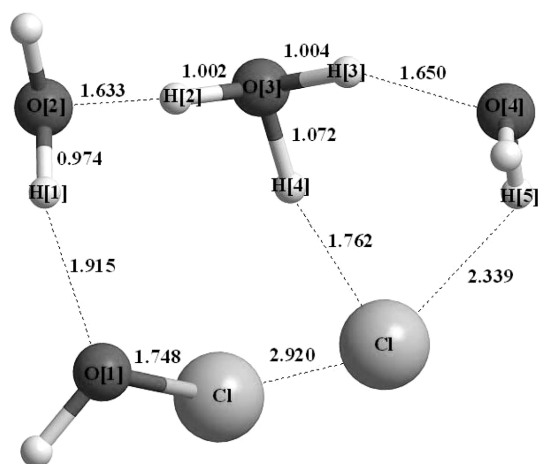
Figure 1. The optimized structure at the MP2/6-31G(d,p) level for the intermediate in $HOCl + 3H_2O + HCl \rightarrow Cl_2 + 4H_2O$ reaction.

affordable cost. The zero-point energy corrected barrier heights and reaction energies calculated at various levels of theory are listed in Table 5. For the reactions with 0 to 2 water molecules (HW0, HW1, and HW2), the barrier height decreases with the number of water molecules. It is over 50 kcal/mol without water, and becomes about 40 and 10 kcal/mol by adding one and two water molecules, respectively. The barrier heights depend on not only the level of theory

but also the size of the basis sets. At the MP2 level, the TZ2P basis sets predicted the lowest barrier height for the HW1 reaction. The barrier heights for HW1 and HW2 from the MP2/6-31G(d,p)//HF/6-31G(d,p) and MPW1K methods are about 20% larger and smaller, respectively, than those from the MP2/6-31G(d,p) method. The MP2/6-31G(d,p) and MPW1K/6-31+G(d,p) values agree very well with the MCCM-UT-CCSD//MP2/6-31G(d,p) and MCG3//MP2/6-31G(d,p) ones, respectively. All multilevel methods predict similar reaction energies for a given reaction (within 2 kcal/mol difference). The MP2 values depend much on the size of basis sets. It varies from –6.8 kcal/mol using 6-31G(d,p) basis sets to –13.0 kcal/mol using cc-pVTZ basis sets. Using the larger basis sets gives closer values to the multilevel results. It is interesting to note that the HF/cc-pVDZ values agree better than the MP2/6-31G(d,p) values with the multilevel results. Since the MCG3 level tends to overestimate the hydrogen bond strength of H_2O dimer,[34] the MCCM-UT-CCSD level seems to predict more reliable value for the reaction energies.

ClONO₂ + H₂O → HONO₂ + HOCl (NW1). The geometrical parameters for reactant complex (RC), transition state (TS), and product complex (PC) calculated at HF and MP2 levels of theory are listed in Table 6. Most geometrical parameters optimized at the HF levels are quite similar. MP2 level predicts longer N-O bonds and shorter hydrogen bonds

Table 5. Barrier Heights and reaction energies[a] at various levels of theory including zero-point energy correction[b]

	HW0	HW1	HW2	HW3
HF/cc-pVDZ	76.7(–14.4)	58.6(–12.2)	32.1(–15.3)	29.2
MP2/6-31G(d,p)	56.8(–9.2)	41.2(–6.8)	13.6(–7.0)	6.14
MP2/6-31+G(d,p)		42.1(–9.2)		
MP2/cc-pVTZ		37.2(–13.0)		
MP2/tz2p		35.8(–12.9)		
MCCM-UT-CCSD	56.1(–17.0)	39.7(–14.3)		
MCCM-UT-CCSD//MP2/6-31G(d,p)	56.7(–16.9)	40.6(–14.4)	13.3(–16.4)	6.7
MCCM-UT-MP4SDQ//MP2/6-31G(d,p)	57.9(–17.0)	40.1(–14.4)	12.9(–16.4)	6.5
MCG3//MP2/6-31G(d,p)	52.8(–17.6)	33.9(–15.6)	10.1(–16.0)	
MC-QCISD//MP2/6-31G(d,p)	33.6(–18.2)	38.0(–16.1)	13.6(–16.2)	
B3LYP/6-31+G (d)[a]	42.2	27.1	6.63	4.12
MPW1K/6-31+G (d,p)[a]	54.7	33.1	9.74	3.28
MP2//HF/6-31+G (d)[b]	55.3	48.3	16.1	14.4

[a]Numbers in parenthesis. [b]Zero-point energies for the multilevel calculations were obtained from the MP2/6-31G(d,p) frequencies.

(O1-H in RC and O3-H in PC) than the HF levels. The characteristics of TS depend very much on the level of theory. The O3-H bond length is changed only 0.027 Å at the HF/6-31G(d,p) level as the reaction goes from RC to TS, whereas it is varied 0.197 Å at the MP2/6-31G(d,p) level. The O1-H bond lengths of TS are 2.274 and 1.347 Å at the HF/6-31G(d,p) and MP2/6-31G(d,p) levels, respectively. The proton on water is hardly transferred toward the nitrate oxygen at the HF level, whereas significant proton transfer is

occurred at the MP2 level. In terms of the proton transfer, the HF level predicts more reactant-like transition state than the MP2 level. The O3-Cl bond lengths of TS are 1.798 and 1.974 Å, which are 0.131 and 0.255 Å larger than those of PC at the HF/6-31G(d,p) and MP2/6-31G(d,p) levels, respectively, suggesting that the HF level predicts more product-like transition state in terms of the Cl-atom transfer than the MP2 level. This transition state, which is reactant-like in terms of the proton transfer and product-like in terms

Table 6. Geometric parameters for RC, TS, PC in $ClONO_2 + H_2O \rightarrow HONO_2 + HOCl$ (NW1)
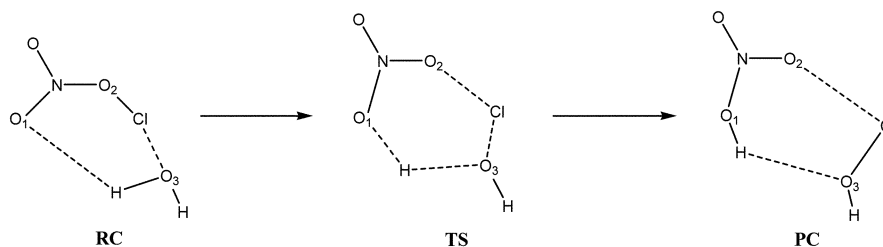
	r_{N-O1}	r_{N-O2}	r_{O2-Cl}	r_{Cl-O3}	r_{O3-H}	r_{H-O1}
			RC			
HF/6-31G(d)[a]	1.175	1.360	1.676	2.682	0.948	
HF/6-31+G(d,p)	1.178	1.365	1.668		0.944	
HF/6-31+G(d)	1.175	1.360	1.676	2.682		
HF/6-31G(d,p)	1.175	1.360	1.675	2.684	0.944	5.135
MP2/6-31G(d,p)	1.209	1.502	1.714	2.671	0.963	4.818
			TS			
HF/6-31G(d)[a]	1.242	1.251	2.376	1.802	0.977	
HF/6-31+G(d)	1.242	1.251	2.379	1.800	0.977	2.262
HF/6-31G(d,p)	1.241	1.251	2.378	1.798	0.971	2.274
MP2/6-31G(d,p)	1.314	1.299	2.179	1.974	1.160	1.347
			PC			
HF/6-31G(d)[a]	1.322	1.195	4.183	1.669	1.892	
HF/6-31+G(d)	1.322	1.195	4.183	1.669	1.892	0.964
HF/6-31G(d,p)	1.322	1.195	4.199	1.667	1.898	0.960
MP2/6-31G(d,p)	1.385	1.236	3.784	1.719	1.804	0.989

[a]Ref. 21

of the Cl-atom transfer, may lead the possible existence of H$_2$OCl$^+$-like moiety in it. The partial charge of H$_2$OCl moiety at the HF level is 0.84, and this value is reduced to 0.71 at the MP2 level. Probably better index for the possible existence of H$_2$OCl$^+$-like moiety would be the dipole moment of TS, which is 11.4 and 4.8 D at the HF and MP2 level, respectively. The H$_2$OCl$^+$ character in the transition state at the HF level seems to be overestimated and may be incorrect. Therefore one should use at least post-HF level of theory to predict the TS correctly.
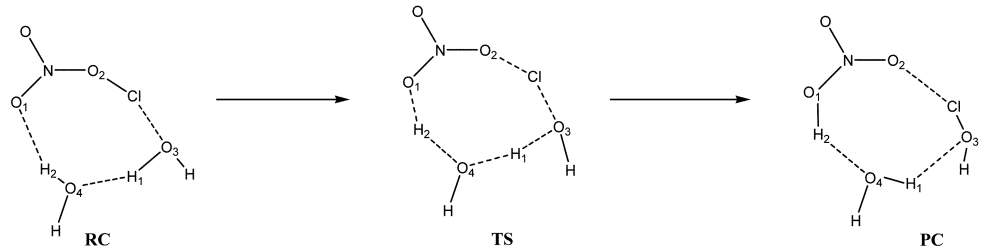
ClONO$_2$ + 2H$_2$O → HONO$_2$ + HOCl + H$_2$O (NW2). The optimized geometrical parameters at HF and MP2 levels are listed in Table 7. MP2 level predicts shorter hydrogen bonds in both RC (O1-H2 and O4-H1) and PC (O3-H1 and O4-H2) than the HF levels. The O4-H2 hydrogen bond in PC is very short, which may form a short and strong hydrogen bond (SSHB). The O2-Cl and O3-Cl distances in the TS at the MP2/6-31G(d,p) level are 0.337 and 0.168 Å larger than those in RC and PC, respectively, which means that the TS is product-like in terms of the Cl-atom transfer. However the O3-H1 distance is 1.436 Å, which means that HOCl-like moiety is present instead of the H$_2$OCl$^+$-like moiety. The O4-H1 and O4-H2 distances are 1.069 and 1.074 Å, respectively, which generates the H$_3$O$^+$-like moiety in the TS. It is interesting to note that the H$_2$OCl$^+$-like moiety present in the TS of the ClONO$_2$ reaction with one water molecule is disappeared and the H$_3$O$^+$-like moiety is

formed by adding one more water molecule. In this case most of the negative charge would be in the NO$_3^-$-like moiety.

ClONO$_2$ + 3H$_2$O → HONO$_2$ + HOCl + 2H$_2$O (NW3). The optimized geometrical parameters of the ClONO$_2$ reaction with three water molecule at HF and MP2 levels are listed in Table 8. As in the previous reaction, MP2 level predicts shorter hydrogen bonds in both RC (O1-H3, O5-H2, and O4-H1) and PC (O3-H1, O5-H3, and O4-H2) than the HF levels. The O5-H3 hydrogen bond in PC is noticeably short, which certainly forms a SSHB. This bond is shorter than the O4-H2 hydrogen bond in the previous reaction (NW2). The TS is product-like in terms of the Cl-atom transfer as the TS in the NW2 reaction. The O5-H3 and H3-O1 distances in TS are 1.010 and 1.531 Å, respectively, which makes the TS reactant-like in terms of the H3-proton transfer. However, the O3-H1 and H1-O4 distances are 1.411 and 1.062 Å, respectively, which makes the TS product-like in terms of the H1-proton transfer. The H2-proton is in between two oxygen atoms O4 and O5, which is closer to O4 but the difference is very small. This result suggests that the H$_5$O$_2^+$-like moiety is formed in the TS at the MP2 level. The HF/6-31G(d,p) level predicts 1.512 Å for the O5-H2 distance, which results in the H$_3$O$^+$-like moiety in the TS. The use of HF level can make incorrect conclusion for the characteristics of transition state in this reaction.
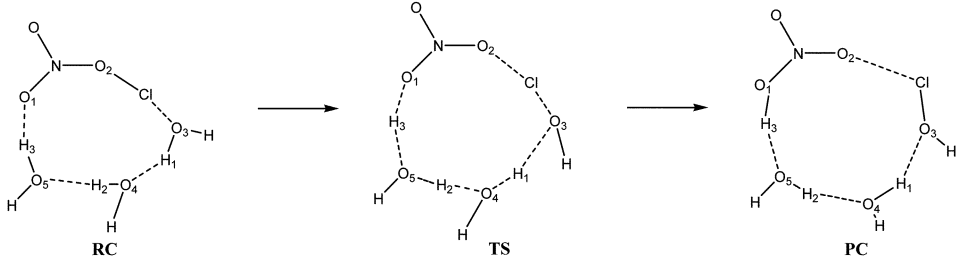
The zero-point energy corrected barrier heights and reac-

Table 7. Geometric parameters for RC, TS, PC in ClONO$_2$ +2H$_2$O → HONO$_2$ + HOCl + H$_2$O (NW2)

	r_{N-O1}	r_{N-O2}	r_{O2-Cl}	r_{Cl-O3}	r_{O3-H1}	r_{H1-O4}	r_{O4-H2}	r_{H2-O1}
					RC			
HF/6-31G(d) [a]	1.182	1.353	1.681	2.593	0.956	1.971	0.950	2.443
HF/6-31+G(d)	1.182	1.353	1.681	2.593	0.965	1.971	0.950	2.443
HF/6-31G(d,p)	1.182	1.353	1.681	2.601	0.951	1.985	0.946	2.469
MP2/6-31G(d,p)	1.216	1.468	1.728	2.523	0.975	1.869	0.966	2.290
					TS			
HF/6-31G(d) [a]	1.236	1.259	2.108	1.802	1.262	1.155	0.989	1.732
HF/6-31+G(d)	1.236	1.259	2.108	1.802	1.262	1.155	0.989	1.732
HF/6-31G(d,p)	1.236	1.259	2.110	1.799	1.247	1.152	0.983	1.718
MP2/6-31G(d,p)	1.286	1.296	2.065	1.885	1.436	1.069	1.074	1.409
					PC			
HF/6-31G(d) [a]	1.312	1.200	3.989	1.668	2.002	0.954	1.721	0.978
HF/6-31+G(d)	1.312	1.200	3.989	1.668	2.002	0.954	1.721	0.978
HF/6-31G(d,p)	1.310	1.200	3.844	1.668	2.028	0.950	1.704	0.974
MP2/6-31G(d,p)	1.363	1.241	3.576	1.717	1.887	0.974	1.618	1.010

[a]Ref. 21

Table 8. Geometric parameters for RC, TS, PC in $ClONO_2 + 3H_2O \rightarrow HONO_2 + HOCl + 2H_2O$ (NW3)

	r_{N-O1}	r_{N-O2}	r_{O2-Cl}	r_{Cl-O3}	r_{O3-H1}	r_{H1-O4}	r_{O4-H2}	r_{H2-O5}	r_{O5-H3}	r_{H3-O1}
					RC					
HF/6-31+G(d,p)[a]	1.184	1.348	1.684	2.596	0.954	1.911	0.952	1.942	0.946	2.207
HF/6-31G(d,p)	1.184	1.346	1.687	2.527	0.955	1.874	0.953	1.910	0.946	2.192
MP2/6-31G(d,p)	1.219	1.447	1.740	2.435	0.983	1.757	0.978	1.795	0.966	2.124
					TS					
HF/6-31+G(d,p)[a]	1.228	1.255	2.136	1.783	1.256	1.123	0.999	1.537	0.963	1.772
HF/6-31G(d,p)	1.226	1.256	2.111	1.790	1.267	1.114	1.004	1.512	0.963	1.755
MP2/6-31G(d,p)	1.272	1.305	2.070	1.877	1.411	1.062	1.156	1.248	1.010	1.531
					PC					
HF/6-31G(d,p)	1.305	1.202	3.789	1.668	2.087	0.949	1.856	0.957	1.642	0.983
MP2/6-31G(d,p)	1.351	1.244	3.570	1.715	1.948	0.972	1.741	0.986	1.530	1.029

[a]Ref. 16

Table 9. Barrier Heights and reaction energies[a] at various levels of theory including zero-point energy correction[b]

	NW1	NW2	NW3
HF/6-31G(d,p)	70.4(–10.4)	35.8(–14.4)	26.1(–15.1)
MP2/6-31G(d,p)	64.1(–1.0)	26.1(–4.3)	16.9(–6.3)
MC-QCISD//MP2/6-31G(d,p)	59.8(–0.7)	26.9(–3.5)	20.6(–4.5)
MCCM-UT-CCSD//MP2/6-31G(d,p)	62.3(–3.1)	25.2(–6.4)	18.2(–7.6)
MCCM-UT-MP4SDQ//MP2/6-31G(d,p)	62.7(–2.3)	25.3(–5.6)	18.3(–6.9)
MP2//HF/6-31+G(d)	68.1	26.2	18.6

[a]Numbers in parenthesis. [b]Zero-point energies for the multilevel calculations were obtained from the MP2/6-31G(d,p) frequencies

tion energies for the reactions with 1 to 3 water molecules (NW1, NW2, and NW3) calculated at various levels of theory are listed in Table 9. The barrier height decreases and the reactions become more exoergic, as the number of water molecules is increased. The results from two multilevel calculations, MCCM-UT-CCSD and MCCM-UT-MP4SDQ, are quite similar with each other. The MP2//HF/6-31+G(d,p) level predicts barrier heights relatively well comparing with the multilevel results except for the NW1 reaction, although it can mislead the structural information of the transition state, which is very important for the reaction dynamics study.

HF level can not correctly predict the TS structure, so the electron correlation should be considered appropriately. In HW3 reaction, the HF level predicts an incorrect mechanism. Previous dual-level calculations, MP2 level single-point energy calculations using the HF level geometry, may contain some errors, so one must interpret them with care. The MP2 level of theory gives quite good results in barrier heights comparing with the MCCM results.

Conclusions

The barrier heights for the proton transfer in HOCl + HCl and H_2O + $ClONO_2$ reactions on water clusters are reduced greatly by adding water molecules. The HF method overestimates and the DFT underestimates the barrier height. The transition state structures and the predicted reaction mechanism depend on the level of theory. In particular, the

References

1. Cicerone, R. J. *Science* **1987**, *237*, 35.
2. Crutzen, P. J.; Arnold, F. *Nature* **1986**, *324*, 651.
3. Farman, J. C.; Gardiner, B. G.; Shanklin, J. D. *Nature* **1985**, *315*, 207.
4. Leu, M. T. *Geophys. Res. Lett.* **1988**, *15*, 17.
5. McElroy, M. B.; Salawitch, R. J.; Wofsy, S. C. *Geophys. Res. Lett.* **1986**, *13*, 1296.
6. Molina, M. J.; Tso, T.; Molina, L. T.; Wang, F. C. *Science* **1987**,

238, 1253.

7. Molina, M. J.; Molina, L. T.; Kolb, C. E. *Annu. Rev. Phys. Chem.* **1996**, *47*, 327.

8. Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *321*, 755.

9. Solomon, S. *Rev. Geophys.* **1988**, *26*, 131.

10. Tolbert, M. A.; Rossi, M. J.; Malhotra, R.; Golden, D. M. *Science* **1987**, *238*, 1258.

11. Toon, O. B.; Kamill, P.; Turco, R. P.; Pinto, J. *Geophys. Res. Lett.* **1986**, *13*, 1284.

12. Wennberg, P. O. *Science* **1994**, *266*, 398.

13. Hanson, D. R. *J. Phys. Chem.* **1995**, *99*, 13059.

14. Sodeau, J. R.; Horn, A. B.; Banham, S. F.; Koch, T. G. *J. Chem. Phys.* **1995**, *99*, 6258.

15. Bianco, R.; Thompson, W. H.; Morita, A.; Hynes, J. T. *J. Phys. Chem. A* **2001**, *105*, 3132.

16. Bianco, R.; Hynes, J. T. *J. Phys. Chem. A* **1998**, *102*, 309.

17. Zhou, Y.-F.; Liu, C.-B. *Int. J. Quantum Chem.* **2000**, *78*, 281.

18. Xu, S. C. *J. Chem. Phys.* **1999**, *111*, 2242.

19. Richardson, S. L.; Francisco, J. S.; Mebel, A. M.; Morokuma, K. *Chem. Phys. Lett.* **1997**, *271*, 395.

20. Liu, Z. F.; Siu, C. K.; Tse, J. S. *Chem. Phys. Lett.* **1999**, *309*, 335.

21. Xu, S. C.; Zhao, X. S. *J. Phys. Chem. A* **1999**, *103*, 2100.

22. Voegele, A. F.; Tautermann, C. S.; Loerting, T.; Liedl, K. R. *J. Phys. Chem. A* **2002**, *106*, 7850.

23. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Rev. A. 9; Gaussian, Inc.: Pittsburgh, PA, 1998.

24. Fast, P. L.; Corchado, J. C.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem.* **1999**, *103*, 5129.

25. Fast, P. L.; Corchado, J. C.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 3139.

26. Fast, P. L.; Sanchez, M. L.; Corchado, J. C.; Truhlar, D. G. *J. Chem. Phys.* **1999**, *110*, 11679.

27. Fast, P. L.; Sanchez, M. L.; Truhlar, D. G. *Chem. Phys. Lett.* **1999**, *306*, 407.

28. Fast, P. L.; Truhlar, D. G. *J. Phys. Chem.* **2000**, *104*, 6111.

29. Tratz, C. M.; Fast, P. L.; Truhlar, D. G. *PhysChemComm* **1999**, *2*, 1.

30. Rodgers, J. M.; Lynch, B. J.; Fast, P. L.; Zhao, Y.; Pu, J.; Chuang, Y.-Y.; Truhlar, D. G. *Multilevel-version 3.1*; University of Minnesota: Minneapolis, MN, 2003.

31. Hiraoka, K.; Takimoto, H.; Yamabe, S. *J. Phys. Chem.* **1986**, *90*, 5910.

32. Valeev, E. F.; Schaefer III, H. F. *J. Chem. Phys.* **1998**, *108*, 7197.

33. Xie, Y.; Remington, R. B.; Schaefer III, H. F. *J. Chem. Phys.* **1994**, *101*, 4878.

34. Park, C.-Y.; Kim, Y.; Kim, Y. *J. Chem. Phys.* **2001**, *115*, 2926.