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Ionic Dissociation of Perchloric Acid in Microsolvated Clusters

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Ionization or ionic dissociation of perchloric acid in the clusters $HClO_4$–$(H_2O)_n$ ($n = 1-3$) and $HClO_4$–NH_3–$(H_2O)_n$ ($n = 0, 1$) is investigated by density functional theory and ab initio molecular orbital theory. The equilibrium structures, binding energies, and dipole moments of the clusters are calculated using the hybrid density functional (B3LYP) method with the 6-31+G* and 6-311++G** basis sets and the second-order Møller−Plesset approximation method with the 6-311++G** basis set. Harmonic vibrational frequencies are obtained from the B3LYP/6-311++G** calculations. Perchloric acid is found to require a minimum of three water molecules for ionization to occur and at least one water molecule to protonate ammonia. The corresponding clusters with fewer water molecules are found to be strongly hydrogen-bonded. The acid strength and the related properties of perchloric acid are discussed and compared to those of sulfuric acid in the context of clusters with ammonia and water.

I. Introduction

Acid ionization and acid−base reactions in aqueous solution are probably among the most fundamental processes in chemistry. A common feature in such processes is the transfer of a proton from the acid to the base molecule such as water or ammonia (the proton acceptor). Solvent (water) molecules clearly play a major role in these processes. While experimental insights into the mechanisms of these processes have been limited, quantum mechanical calculations have become a powerful unique tool for investigating such mechanisms in great detail at the molecular level. The mechanisms of ionic dissociation and acid−base reactions have been investigated by computational studies using molecular clusters consisting of the relevant acid, base (proton acceptor), and solvent molecules.[1−6] The size of the cluster for a given acid or an acid−base pair can be progressively enlarged by adding individual solvent molecules. These studies focus on the specific roles that the individual solvent molecules play and on the minimum number of solvent molecules that are required to cause the ionization of the acid or the transfer of a proton from the acid to the base, a phenomenon that is normally observed or assumed to take place in a liquid solution.

Hydrated clusters involving hydrogen halides (HF and HCl) and H_2S have been shown to require four or more water molecules for ionization to occur.[1] Specifically, hydrogen bromide (HBr) has been shown to have partial ionization with three water molecules and complete ionization with four water molecules.[2] Ionization of sulfuric acid (H_2SO_4) occurs with as few as three water molecules.[3,4] Ionization of nitric acid (HNO_3) occurs with five water molecules in the cluster.[5] In all of these cases one water molecule acts as a proton acceptor while the other water molecules act to stabilize the newly formed ions.

The acid−base neutralization reactions of nitric acid, hydrogen chloride, and sulfuric acid with ammonia in water clusters have also been studied.[6−8] Although ammonia is regarded as a reasonably strong base, all of the acid−ammonia pairs studied so far show only as hydrogen-bonded complexes in the absence of solvent molecules. Proton transfer occurs for nitric acid−ammonia in a cluster with at least three water molecules,[6] for hydrogen chloride−ammonia with two water molecules,[7] and for sulfuric acid−ammonia with only a single water molecule.[8]

All of the clusters mentioned appear to establish the trend that the number of water molecules required for ionization decreases as the acid considered increases in acidity. It is natural then to look at an acid that is considered somewhat stronger than sulfuric acid, the strongest acid previously studied using the approach of clusters. Perchloric acid ($HClO_4$) is widely considered a stronger acid. In this work, we will examine the clusters of perchloric acid with a varying number of water molecules and the clusters of perchloric acid−ammonia with and without water. The equilibrium geometries, dipole moments, binding energies, and harmonic frequencies for the clusters will be calculated and compared to the corresponding clusters involving sulfuric acid. It would be important for us to analyze any effect of the stronger acid on the properties of the clusters and the number of solvent water molecules required for ionization or proton transfer within a cluster.

Perchloric acid may be important in atmospheric chemistry as well. Svensson et al.[9] have suggested that perchloric acid may represent an important sink for chlorine between 15 and 20 km above the Earth's surface. Jaegle et al.[10] have also suggested that sulfate aerosol particles may oxidize ClO and form $HClO_4$, as HCl and $HClO_4$ have been observed in the reaction of ClO on sulfuric acid.[11] Characterization of the molecular properties for the clusters containing $HClO_4$ may therefore provide valuable insights into the role and significance of the acid in atmospheric chemistry.

II. Theoretical Method

The equilibrium geometries of the molecular clusters considered in this work were optimized by density functional theory (DFT) and ab initio methods. The DFT method used was the popular Becke three-parameter functional[12−14] with the nonlocal correlation provided by Lee, Yang, and Parr (B3LYP).[15] The ab initio method was frozen-core second-order Møller−Plesset

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perturbation approximation (MP2).[16,17] Both of the methods are known to be reliable, particularly for calculating closed-shell stable molecules and hydrogen-bonded complexes.[15,16] All calculations used a reasonably large basis set, 6-311++G(d,p), and were carried out with the Gaussian 98 program package.[18]

The molecular clusters $HClO_4$–$(H_2O)_n$ ($n = 1-3$) and $HClO_4$–NH_3–$(H_2O)_n$ ($n = 0, 1$) were constructed from the three monomers, $HClO_4$, NH_3, and H_2O. The equilibrium geometries for the monomers and for the clusters were obtained by full optimization using analytic gradients. Our primary focus was on the most stable configuration for each cluster, although other configurations of competing stability were also examined. Generally, the most stable configuration for a cluster contains the strongest possible hydrogen bonding between the monomers. For the larger clusters where the most stable configurations are not obvious, additional calculations were performed on likely candidates to determine the most stable geometry. Our results and discussions, however, are focused on the most stable configuration for each cluster, although less stable configurations are mentioned for comparison.

The binding energies of the clusters were also calculated to compare the stability of the clusters with respect to the separate molecules. For a given cluster, the binding energy, D_e, was determined as a difference between the total energy of the cluster and the sum of the total energies of the isolated monomers ($HClO_4$, NH_3, and n-H_2O) contained in the cluster. Harmonic vibrational frequencies and IR intensities for all clusters were obtained from B3LYP calculations. Zero-point energy-corrected binding energies, D_0, were obtained using the calculated harmonic frequencies. No corrections were made to D_e for the basis set superposition error (BSSE). The effect of BSSE is expected to be relatively small as compared to the binding energy for a strongly hydrogen-bonded system such as $HClO_4$–NH_3–$(H_2O)_n$. A previous study[5] on a similar system, NH_3–HNO_3, using the same method showed that the BSSE contribution was less than 0.4 kcal/mol, compared to a value of 14 kcal/mol for the binding energy D_e.

III. Results and Discussion

Figures 1 and 2 show side views of the equilibrium structures for the clusters $HClO_4$–$(H_2O)_n$ ($n = 1-3$) and $HClO_4$–NH_3–$(H_2O)_n$ ($n = 0, 1$), respectively. Table 1 gives the bond distances, bond angles, dipole moments, and total energies of the relevant monomers (NH_3, NH_4^+, $HClO_4$, ClO_4^-, H_2O, and H_3O^+), compared with available experimental data.[19,20] Tables 2 and 3 present selected bond lengths and molecular properties of the two cluster series, $HClO_4$–$(H_2O)_n$ ($n = 1-3$) and $HClO_4$–NH_3–$(H_2O)_n$ ($n = 0, 1$), respectively. It is clear from the tables that the B3LYP and MP2 calculations are consistent with each other. Nevertheless, the following discussions of these results are primarily based on the MP2 values. Table 4 presents the harmonic vibrational frequencies and infrared intensities for the intramolecular modes of the clusters from B3LYP calculations, compared to and correlated with those of $HClO_4$, ClO_4^-, H_3O^+, and NH_4^+, along with available experimental values.[20] Note that the frequencies for the monomers H_2O and NH_3 are reported elsewhere[4,8] and the corresponding intramolecular frequencies are not significantly different from these monomer frequencies.

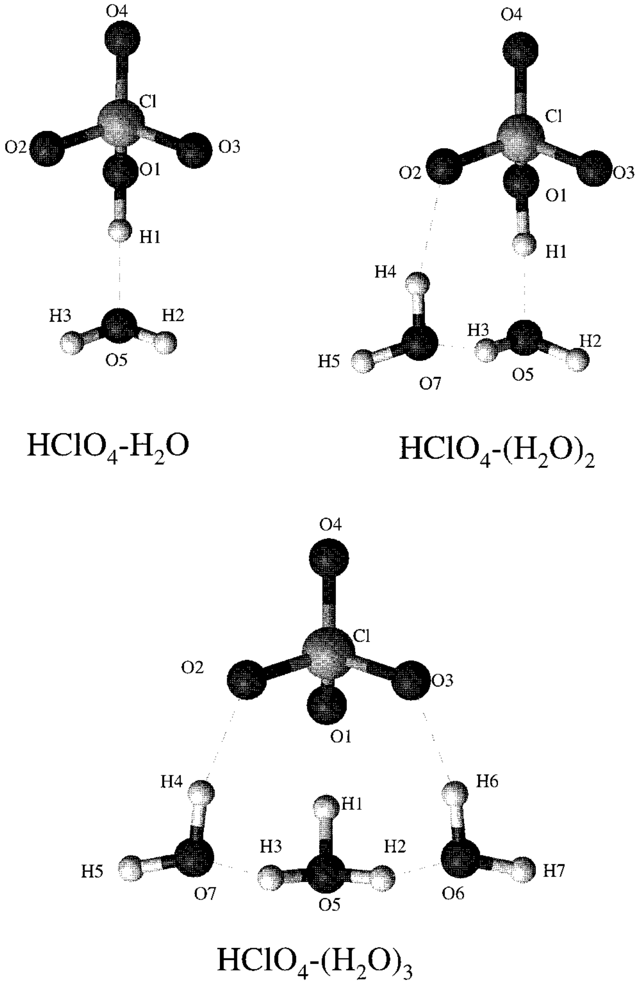

Figure 1. Equilibrium geometries for the clusters $HClO_4$–$(H_2O)_n$ ($n = 1-3$) from B3LYP calculations.

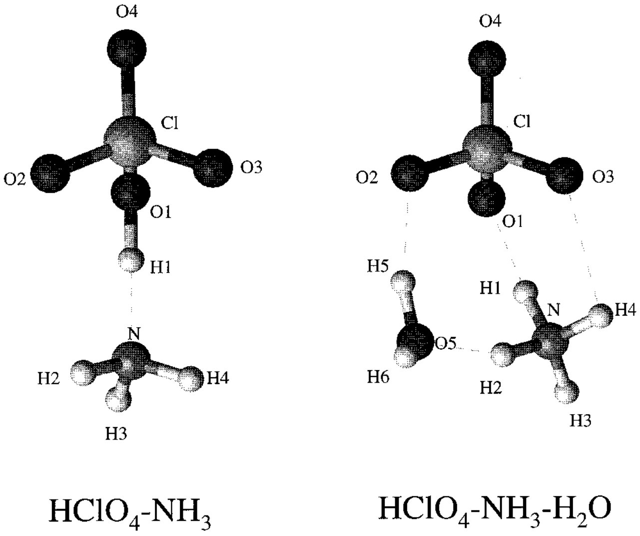

Figure 2. Equilibrium geometries for the clusters $HClO_4$–NH_3–$(H_2O)_n$ ($n = 0, 1$) from B3LYP calculations.

Monomers. As shown in Tables 1 and 4, the equilibrium geometry and molecular properties calculated for perchloric acid are in reasonable agreement with experiment values.[21] The hydrogen atom of $HClO_4$ is staggered from the rest of the molecule, and the base of the molecule (ClO_3) is close to C_{3v} symmetry. The equilibrium geometry is also in agreement with previous calculations.[22,23] The equilibrium geometries for water and ammonia are also in good agreement with experiment.[8] The calculated dipole moments are overestimated, but are consistent with the level of theory and basis sets used in this study.[6]

The calculated harmonic frequencies of perchloric acid agree reasonably with available experimental values and with the MP2

TABLE 1: Equilibrium Bond Distances (Å), Bond Angles (deg), Dipole Moments (D), and Total Energies (hartrees) Calculated for Monomeric $HClO_4$, ClO_4^-, H_2O, H_3O^+, NH_3, and NH_4^+ from Different Calculations and Experiment

molecule[a]	param	B3LYP	MP2	exptl[b]
$HClO_4$ (C_s)	r(O1H)	0.974	0.973	0.98[c]
	r(ClO1)	1.726	1.704	1.641
	r(ClO2)	1.460	1.439	1.414
	r(ClO3)	1.460	1.439	1.414
	r(ClO4)	1.449	1.429	1.404
	∠(ClO1H)	105.5	105.4	105.0
	μ	2.28	2.08	
	E	−761.41835	−759.15290	
ClO_4^- (T_d)	r(ClO)	1.501	1.476	
	∠(OClO)	109.500	109.5	
	μ	0.00	0.00	
	E	−760.93252	−758.68037	
H_2O (C_{2v})	r(OH)	0.980	0.978	0.957
	∠(HOH)	113.5	112.1	104.5
	μ	2.16	2.26	1.94
	E	−76.45853	−76.05260	
H_3O^+ (C_{3v})	r(OH)	0.980	0.978	
	∠(HOH)	113.5	112.1	
	μ	1.44	1.57	
NH_3 (C_{3v})	r(NH)	1.015	1.013	1.012
	∠(HNH)	107.8	107.4	106.7
	μ	1.69	1.73	1.51
	E	−56.58272	−56.21435	
NH_4^+ (T_d)	r(NH)	1.026	1.024	
	∠(HNH)	109.5	109.5	
	μ	0.00	0.00	
	E	−56.92036	−56.75569	

[a] Some of the atomic labels have been omitted due to uniqueness or symmetry. [b] Experimental values for NH_3 and H_2O are from ref 19, and those for $HClO_4$ are from ref 22. [c] Not refined.

TABLE 2: Equilibrium Bond Lengths (Å), Rotational Constants *A*, *B*, and *C* (GHz), Binding Energies D_e (kcal/mol), and Dipole Moments μ (D) of the $HClO_4$–$(H_2O)_n$ (n = 1−3) System from B3LYP and MP2 Calculations

	$HClO_4$–H_2O		$HClO_4$–$(H_2O)_2$		$HClO_4$–$(H_2O)_3$	
param	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
r(O1H1)	1.002	0.995	1.031	1.019	1.549	1.497
r(H1O5)	1.679	1.696	1.536	1.551	1.026	1.030
r(ClO1)	1.684	1.655	1.637	1.631	1.536	1.514
r(ClO2)	1.466	1.444	1.478	1.455	1.502	1.477
r(ClO3)	1.466	1.445	1.464	1.443	1.502	1.477
r(ClO4)	1.451	1.430	1.450	1.430	1.458	1.437
r(H2O5)	0.964	0.962	0.963	0.961	1.023	1.012
r(H3O5)	0.964	0.962	0.985	0.978	1.023	1.012
r(O7H3)			1.746	1.765	1.550	1.560
r(O7H4)			0.970	0.966	0.980	0.976
r(O7H5)			0.962	0.960	0.963	0.961
r(O2H4)			2.018	2.014	1.832	1.832
r(O6H2)					1.550	0.960
r(O6H6)					0.980	0.976
r(O6H7)					0.963	0.961
r(O3H6)					1.832	1.832
A	4.954	5.099	3.027	3.093	1.813	1.845
B	1.843	1.964	1.259	1.290	1.085	1.103
C	1.816	1.934	1.082	1.107	0.861	0.878
μ	4.66	4.10	4.08	3.76	5.79	5.6
D_e	12.0	13.9	24.5	24.0	37.7	34.3

values by Francisco et al.[23] The experimental frequencies that were compared in the early theoretical study[23] were inaccurate due to Cl_2O_7 impurities.[24] A procedure was developed to remove the Cl_2O_7 impurities and resulted in more reliable experimental frequencies for the ν_2, ν_3, ν_9, and ν_{11} modes shown in Table 4.[25] This indicates the degree of uncertainty and challenge in determining the spectral data for perchloric acid as the acid is highly reactive and unstable.

TABLE 3: Equilibrium Bond Lengths (Å), Rotational Constants *A*, *B*, and *C* (GHz), Binding Energies D_e (kcal/mol), and Dipole Moments μ (D) of the $HClO_4$–NH_3–$(H_2O)_n$ (n = 0, 1) from B3LYP and MP2 Calculations

	$HClO_4$–NH_3		$HClO_4$–NH_3–H_2O	
param	B3LYP	MP2	B3LYP	MP2
r(NH1)	1.582	1.582	1.061	1.061
r(NH2)	1.016	1.016	1.052	1.047
r(NH3)	1.017	1.017	1.017	1.016
r(NH4)	1.017	1.017	1.022	1.019
r(ClO1)	1.657	1.632	1.532	1.507
r(ClO2)	1.454	1.432	1.462	1.441
r(ClO3)	1.469	1.447	1.501	1.477
r(ClO4)	1.470	1.445	1.505	1.480
r(O1H1)	1.049	1.033	1.676	1.629
r(O3H4)	3.456	3.102	2.406	2.478
r(O5H5)			0.983	0.978
r(O5H6)			0.962	0.960
r(O5H2)			1.711	1.698
r(O2H5)			1.820	1.816
A	4.977	5.126	3.037	3.105
B	1.845	1.956	1.428	1.463
C	1.822	1.930	1.197	1.223
μ	6.40	5.81	9.23	9.21
D_e	17.0	17.8	32.6	35.5

$HClO_4$–$(H_2O)_n$ Structures. A strong hydrogen bond forms in $HClO_4$–H_2O as the first water is introduced to perchloric acid. The acid acts as a hydrogen bond donor while the water acts as an acceptor in this monohydrated cluster. The interaction between perchloric acid and water is highly strong and rigid, with a short and nearly linear O−H···O hydrogen bond. The strong hydrogen bonding of perchloric acid to water is also evidenced by the increase of the acidic OH bond distance, r(O1H1), from 0.973 to 0.995 Å, accompanied by a red shift in the OH stretching frequency and a sharp increase in IR intensity (to be discussed in detail later). The binding energy between the acid and the water in $HClO_4$–H_2O is 13.9 kcal/mol at the MP2 level (12.0 kcal/mol at B3LYP). It should be noted that two possible equilibrium structures are observed for this cluster that are very similar in energy. The structural difference arises from the orientation of the water molecule, having one pointing away from the O atoms of perchloric acid and the other pointing toward the O atoms. The slightly more stable structure, as reported, can lead to the ionic dissociation of the acid by adding two more water molecules while the other structure cannot lead to the dissociation.

In the dihydrated cluster, $HClO_4$–$(H_2O)_2$, the second water molecule is oriented in such a way that it accepts a hydrogen bond from the first water while donating a hydrogen bond to an oxygen atom of perchloric acid. As a result, a cyclic hydrogen bond ring structure is established. The bond distance between the H atom of $HClO_4$ and the O atom of the first water, r(H1O5), decreases to 1.551 Å from 1.696 Å for $HClO_4$–H_2O, while the O−H covalent bond distance of $HClO_4$, r(O1H1), increases further to 1.019 Å from 0.995 Å for $HClO_4$–H_2O. This indicates that the hydrogen bond of the $HClO_4$–H_2O unit in $HClO_4$–$(H_2O)_2$ is further strengthened while the O−H covalent bond of $HClO_4$ is weakened. There are two additional hydrogen bonds in $HClO_4$–$(H_2O)_2$. One is between the first and second water molecules. The bond distance r(O7H3) = 1.77 Å indicates that it is nearly as strong as the hydrogen bond for $HClO_4$–H_2O. The other hydrogen bond is between the second water and the oxygen of perchloric acid. The bond distance r(O2H4) = 2.01 Å indicates it is a weaker and more typical hydrogen bond. The binding energy for $HClO_4$–$(H_2O)_2$ is over 10 kcal/mol larger than that for $HClO_4$–H_2O, consistent with the existence of two

TABLE 4: Harmonic Frequencies (cm^{-1}) and Infrared Intensities (km/mol, in Parentheses) of $HClO_4{-}(H_2O)_n$ ($n = 0-3$) and $HClO_4{-}NH_3{-}(H_2O)_n$ ($n = 0, 1$) from B3LYP Calculations, Correlated by Monomer Vibrational Modes

monomer		freq for monomer		freq for $HClO_4{-}(H_2O)_n$			freq for $HClO_4{-}NH_3{-}(H_2O)_n$	
mode	approx descriptn	calcd	exptl	$n = 1$	$n = 2$	$n = 3$	$n = 0$	$n = 1$
				$HClO_4$[a]				
ν_1 (a)	OH str	3707 (133)	3553	3181 (1339)	2548 (2189)		2349 (3004)	
ν_2 (a)	ClO asym str	1122 (269)	1326	1101 (308)	1107 (208)		1075 (110)	
ν_3 (a)	HOCl bend	1118 (146)	1201	1376 (91)	1474 (90)		1538 (70)	
ν_4 (a)	ClO sym str	936 (93)	1048	928 (121)	897 (117)		921 (166)	
v_5 (a)	Cl−OH str	644 (169)	726	671 (158)	694 (130)		692 (5)	
ν_6 (a)	OClO asym def	518 (27)	582	523 (10)	532 (17)		535 (4)	
ν_7 (a)	OClO sym def	478 (1)	555	498 (8)	512 (34)		518 (22)	
ν_8 (a)	ClO3 rock	357 (4)	421	366 (0)	363 (1)		391 (3)	
ν_9 (b)	ClO asym str	1232 (156)	1265	1134 (220)	1041 (205)		1128 (278)	
ν_{10} (b)	OClO asym def	514 (25)	582	524 (21)	576 (84)		528 (23)	
ν_{11} (b)	ClO3 rock	363 (20)	421	386 (3)	397 (43)		372 (45)	
ν_{12} (b)	OH torsion	179 (86)		895 (75)	943 (239)		1131 (262)	
ClO_4^-								
ν_1(e)	*d*-str	397 (16)				413 (18)		387 (11)
						418 (10)		434 (15)
ν_2(t)	*d*-def	555 (21)				551 (20)		549 (22)
						562 (10)		551 (19)
						571 (685)		568 (32)
ν_3 (a_1)	sym str	806 (6)				791 (170)		794 (76)
ν_4 (t)	*d*-def	971 (359)				959 (368)		1084 (346)
						937 (78)		957 (300)
						850 (239)		900 (299)
				H_3O^+				
ν_1	sym def	765 (518)				764 (5)		
ν_2	*d*-def	1673 (121)				1789 (87)		
		1673 (121)				1734 (47)		
ν_3	sym str	3584 (40)				2947 (881)		
ν_4	*d*-str	3680 (498)				2658 (1406)		
		3680 (498)				2727 (2045)		
				NH_4^{+}[b]				
ν_1 (a_1)	sym str	3371 (7)	3115					3478 (116)
ν_2 (e)	*d*-def	1728 (2)	1638					1738 (44)
								1730 (36)
ν_3 (t)	*d*-str	3475 (183)	3250					3572 (85)
								2975 (805)
								2827 (968)
ν_4 (t)	*d*-def	1490 (163)	1398					1412 (61)
								1484 (100)
								1591 (283)

[a] Experimental frequencies from refs 21, 24, and 25. [b] Experimental frequencies in solid NH_4VO_3 from ref 26.

additional hydrogen bonds in $HClO_4{-}(H_2O)_2$. Note that the second water removes the C_s symmetry in the $HClO_4{-}H_2O$ unit.

The equilibrium structure for the trihydrated cluster, $HClO_4{-}(H_2O)_3$, is drastically different from that for the smaller clusters discussed above. The perchloric acid in $HClO_4{-}(H_2O)_3$ is spontaneously dissociated into hydrated ions. The third water takes a position at the opposite side of the $HClO_4{-}H_2O$ unit from the second water, donating a hydrogen bond to the O3 atom of $HClO_4$ and restoring the C_s symmetry to the system. The O1H1 bond distance increases from 1.02 to 1.50 Å while the H1O5 bond distance decreases from 1.55 to 1.03 Å as a result of the addition of the third water. It is clear that the O1H1 covalent bond no longer exists and a new O5H1 covalent bond is formed. The ion pairs ClO_4^- and H_3O^+ form as a proton is transferred from $HClO_4$ to H_2O. The formation of the ion pair is also indicated by an increase in the dipole moment, from 4.10 to 5.63 D, as well as the significant departure of the O1−H1−O5 unit from linearity expected for a typical hydrogen bond. A large binding energy is calculated for $HClO_4{-}(H_2O)_3$, about 10 kcal/mol larger than that for $HClO_4{-}(H_2O)_2$. This is consistent with the stable structure of $HClO_4{-}(H_2O)_3$ that displays favorable interactions of ion pair and polar water molecules.

$HClO_4{-}NH_3{-}(H_2O)_n$ Structures. Perchloric acid is a very strong acid, and ammonia is a reasonably strong base. Surprisingly, the union of the two, $HClO_4{-}NH_3$, exists only as a strongly hydrogen-bonded complex, with $HClO_4$ acting as the hydrogen bond donor and NH_3 as the acceptor. The hydrogen bond distance, $r(NH1) = 1.582$ Å, is shorter than $r(H1O5) = 1.696$ Å for $HClO_4{-}H_2O$ and is comparable to that of the sulfuric acid−ammonia cluster (1.579 Å).[10] The O−H covalent bond distance, $r(O1H1) = 1.033$ Å, is about 0.06 Å longer than the O−H bond distance of $HClO_4$.

In the monohydrated cluster, $HClO_4{-}NH_3{-}H_2O$, a drastic change in geometry takes place at the $HClO_4{-}NH_3$ unit. The introduction of one water molecule to $HClO_4{-}NH_3$ facilitates the proton transfer from $HClO_4$ to NH_3, forming the ion pair $NH_4^+ \cdots ClO_4^-$. The water molecule is so orientated that a H atom connects to an oxygen atom (O4) of ClO_4^- while the O atom of H_2O connects to a H atom of NH_3. The r(O1H1) distance increases from 1.033 to 1.629 Å and the distance r(NH1) decreases from 1.582 to 1.061 Å as a result of the addition of the H_2O molecule. Clearly, the O−H covalent bond of $HClO_4$ no longer exists, and a new NH1 covalent bond is formed. The NH_3 unit rotates noticeably as it converts to the NH_4^+ cation, and multiple hydrogen bonds form in the $HClO_4{-}NH_3{-}H_2O$

TABLE 5: Comparison of Selected Bond Lengths (Å), Binding Energies (kcal/mol), Harmonic Frequencies (cm^{-1}) and Infrared Intensity (km/mol, in Parentheses) for the Clusters $HClO_4-H_2O$, $H_2SO_4-H_2O$,[a] $HClO_4-NH_3-(H_2O)_n$ ($n = 0, 1$) and $H_2SO_4-NH_3-(H_2O)_n$ ($n = 0, 1$)[b]

param	theory	$HClO_4$	H_2SO_4	$HClO_4-H_2O$	$H_2SO_4-H_2O$	$HClO_4-NH_3$	$H_2SO_4-NH_3$	$HClO_4-NH_3-H_2O$	$H_2SO_4-NH_3-H_2O$
r(O1H1)	B3LYP	0.974	0.970	1.002	0.999	1.049	1.043	1.676	1.464
	MP2	0.973	0.968	0.995	0.992	1.033	1.035	1.629	1.444
r(H1O5)	B3LYP			1.679	1.692				
	MP2			1.696	1.701				
r(H1N)	B3LYP					1.582	1.586	1.061	1.106
	MP2					1.582	1.579	1.061	1.105
$\angle$(O−H···O(N))	B3LYP			175	163	179	173	158	177
D_e	B3LYP			12.0	12.4	17.0	16.5	32.6	30.3
	MP2			13.9	13.3	17.8	16.4	35.5	35.5
D_0	B3LYP			9.98	10.2	15.1	14.7	26.7	25.37
ν_1 OH stretch	B3LYP	3707 (133)	3757 (198)	3181 (1339)	3199 (1214)	2349 (3004)	2538 (2863)		
ν_1 red shift	B3LYP			526	502	1358	1256		
ν_1 IR ratio	B3LYP			10	6	23	14		
ν_{12} OH torsion	B3LYP	179 (86)	260 (78)	895 (75)	827 (75)	1131 (262)	1137 (140)		
ν_{12} blue shift	B3LYP			716	567	952	877		
ν_3 HO···Cl(S) bend	B3LYP	1118 (146)	1128 (96)	1376 (91)	1310 (102)	1538 (70)	1491 (114)		
ν_3 blue shift	B3LYP			258	182	420	363		

[a] Reference 4. [b] Reference 8.

cluster. The ClO_4^- unit also rotates to maximize the electrostatic interaction with NH_4^+. The rotations of NH_4^+ and ClO_4^- are shown by the change in the distance between the O4 and H4 atoms. This distance decreases from 3.456 Å in $HClO_4-NH_3$ to 2.406 Å in $HClO_4-NH_3-H_2O$. The rotations would not be possible if the structure of the cluster were dominated by hydrogen bonding. The formation of the ion pair $NH_4^+ \cdots ClO_4^-$ in $HClO_4-NH_3-H_2O$ is evidenced by a sharp increase in dipole moment, from 5.81 D for $HClO_4-NH_3$ to 9.21 D $HClO_4-NH_3-H_2O$. The binding energy is $D_e = 17.8$ kcal/mol for $HClO_4-NH_3$ and $D_e = 35.5$ kcal/mol for $HClO_4-NH_3-H_2O$. The addition of the water molecule results in an increase of 17.7 kcal/mol in D_e.

$HClO_4-(H_2O)_n$ and $HClO_4-NH_3-(H_2O)_n$ Frequencies. With some exceptions, there are no significant changes in the intramolecular vibrational frequencies for the clusters $HClO_4-H_2O$, $HClO_4-(H_2O)_2$, and $HClO_4-NH_3$ from those for the isolated monomers. This supports the equilibrium structures and the fact that no significant changes in bonding take place in the clusters from the monomers. The exceptions are all related to the vibrational modes involving the H atom of $HClO_4$. Three specific modes are involved: the OH stretching (ν_1), the HOCl bending (ν_3), and the O−H torsion (ν_{12}), all of which result in significant changes in frequency from the monomer to the clusters. In the cluster $HClO_4-H_2O$, the OH stretching mode shifts from 3707 to 3181 cm^{-1} while IR intensity increases by an order of magnitude. For $HClO_4-(H_2O)_2$, the OH stretching mode further shifts to 2548 cm^{-1}, with a 2-fold enhancement in IR intensity. Similarly, the OH stretching mode for $HClO_4-NH_3$ shifts to 2349 cm^{-1} with a 23-fold enhancement in IR intensity. This is consistent with the weakening of the OH bond in these clusters as a result of strong hydrogen bonding. On the other hand, the bending and torsional modes for perchloric acid undergo significant blue shifts in these clusters. More specifically, the HOCl bending frequency (ν_3) increases from 1118 cm^{-1} for the $HClO_4$ monomer to 1376, 1474, and 1538 cm^{-1} for $HClO_4-H_2O$, $HClO_4-(H_2O)_2$, and $HClO_4-NH_3$, respectively. Similarly, the OH torsional frequency (ν_{12}) increases from 179 cm^{-1} for $HClO_4$ to 895, 943, and 1131 cm^{-1} for $HClO_4-H_2O$, $HClO_4-(H_2O)_2$, and $HClO_4-NH_3$, respectively. All of these suggest the presence of strong hydrogen bonding. Both of the bending and torsional motions for the H atom of $HClO_4$ in the clusters become hindered as a result of hydrogen bonding, thereby increasing the bending and torsional force constants.

The harmonic frequencies of intramolecular modes for the clusters $HClO_4-(H_2O)_3$ and $HClO_4-NH_3-H_2O$ are found difficult to match to the frequencies of the monomers $HClO_4$, H_2O, and NH_3. The most noticeable change is the disappearance of the OH stretching mode and the related bending of the torsional modes. While the intramolecular harmonic frequencies cannot be fully correlated with the isolated monomer modes for $HClO_4$, H_2O, and NH_3, they can be more easily correlated with those of the ions ClO_4^-, NH_4^+, and H_3O^+, as shown in Table 4. This is consistent with the fact that the ionic dissociation of $HClO_4$ has occurred in the clusters $HClO_4-(H_2O)_3$ and $HClO_4-NH_3-H_2O$.

IV. Comparison to Sulfuric Acid

It is interesting to compare the clusters of perchloric acid with the corresponding clusters of sulfuric acid. The hydrated clusters of H_2SO_4 with up to five water molecules were studied by Re et al.[3] using the B3LYP/D95++** method and by Larson et al.[4] using the B3LYP and MP2 methods with the 6-311++G(d,p) basis set. The clusters of $H_2SO_4-NH_3$ with up to two water molecules were studied by Larson and Tao[8] using the B3LYP and MP2 methods with the 6-311++G(d,p) basis set. Our comparisons of the clusters between $HClO_4$ and H_2SO_4 focus primarily on the geometrical parameters and vibrational frequencies involving the acidic proton that donates a hydrogen bond to water or ammonia in the clusters. It may help us better understand the relative acidity between the two strong acids in aqueous conditions. Table 5 gives a summary of the comparisons between the two series of clusters for $HClO_4$ and H_2SO_4.

The two acids have very comparable OH bond distances in the monomers from B3LYP and MP2 calculations. Upon hydrogen bonding to water, the OH bond distances are both increased by a small, but nearly the same, magnitude. The increases in the OH bond distances are larger upon hydrogen bonding to ammonia than to water, but are nearly the same in magnitude between the two acids. Therefore, the changes in the OH bond lengths upon hydrogen bonding do not yield clear evidence to show the difference in acidity between the two acids. The same conclusion can be drawn from the comparison of the hydrogen bond distances r(H1O5) for the case of bonding to water and r(H1N) for the case of bonding to ammonia. The hydrogen bond distances are shorter in the ammonia systems than in the water systems, but virtually the same between the two acids, with either water or ammonia.

The two acids have nearly the same harmonic frequencies for the OH stretching mode in the monomers from B3LYP calculations. Large red shifts in the frequencies result from hydrogen bonding with water or ammonia, along with large enhancement in IR intensities. However, the $HClO_4$ acid gives a larger red shift than H_2SO_4, and the difference is more pronounced in the hydrogen-bonded systems with ammonia. This indicates that the weakening of the OH bond of $HClO_4$ is more severe than that of H_2SO_4 as the acid interacts with the proton acceptor (water or ammonia). In other words, $HClO_4$ is more acidic than H_2SO_4.

Proton transfer takes place in both $HClO_4$–NH_3–H_2O and H_2SO_4–NH_3–H_2O, producing the distinct cation NH_4^+ and the corresponding anions ClO_4^- and HSO_4^-, respectively. This is demonstrated by the bond distances r(O1H1) and r(H1N). However, there are considerable differences in the bond distances between the two systems. r(O1H1) = 1.629 Å for $HClO_4$–NH_3–H_2O is about 0.2 Å larger than that for H_2SO_4–NH_3–H_2O. On the other hand, r(H1N) = 1.061 Å for $HClO_4$–NH_3–H_2O is about 0.05 Å smaller than that for H_2SO_4–NH_3–H_2O. In each of the systems, the NH_4^+ cation becomes a Lewis acid and the anion (ClO_4^- or HSO_4^-) becomes a Lewis base. The larger r(O1H1) distance for $HClO_4$–NH_3–H_2O than for H_2SO_4–NH_3–H_2O indicates that ClO_4^- is a weaker base than HSO_4^-. The same conclusion can be drawn from the difference in r(H1N) between the two systems. That ClO_4^- is a weaker base than HSO_4^- corresponds to $HClO_4$ being a stronger conjugated acid than H_2SO_4. It is thus clear that the structures of $HClO_4$–NH_3–H_2O and H_2SO_4–NH_3–H_2O provide further strong evidence that $HClO_4$ is a stronger acid than H_2SO_4.

The binding energies for the clusters involving $HClO_4$ are consistently larger than those for the corresponding clusters involving H_2SO_4. In general, the strength of a hydrogen bond formed between an acid and a base molecule, measured by the binding energy D_e of the resulting hydrogen-bonded clusters, increases with the acidity of the acid, or the hydrogen bond donor. Consequently, the larger values of D_e for the clusters involving $HClO_4$ than the corresponding values for H_2SO_4 further show that $HClO_4$ is the stronger acid.

In summary, the comparisons consistently show that $HClO_4$ is a stronger acid than H_2SO_4, despite the insignificant differences in the structures of the monomers and clusters between the two acids. It should be pointed out that gas-phase deprotonization energies[20] calculated at the B3LYP/6-311++G(d,p) level also reflect the subtle difference in acidic strength between $HClO_4$ (300 kcal/mol) and H_2SO_4 (308 kcal/mol).

V. Conclusions

The equilibrium structures and other molecular properties are calculated for the clusters $HClO_4$–$(H_2O)_n$ ($n = 1-3$) and $HClO_4$–NH_3–$(H_2O)_n$ ($n = 0, 1$) using the B3LYP density functional method and MP2 ab initio method with extended basis sets. The clusters of $HClO_4$ with less than three water molecules are all strongly hydrogen-bonded. The $HClO_4$ molecule dissociates in the cluster with three water molecules and produces the H_3O^+ and ClO_4^- ion pair. The $HClO_4$–NH_3 system is also hydrogen-bonded while $HClO_4$–NH_3–H_2O contains the NH_4^+ and ClO_4^- ion pair. The binding energies, dipole moments, and harmonic vibrational frequencies of the clusters provide further support for the equilibrium structures.

Perchloric acid is very similar in acidity to sulfuric acid. The two acid molecules have very comparable OH bond distances and associated vibrational frequencies. They also result in nearly the same hydrogen bond structure with water and ammonia. However, the vibrational frequencies involving the acidic H atom in the hydrogen-bonded clusters and the ion pair structures in larger clusters, along with the binding energies of the various clusters, consistently show that $HClO_4$ is a stronger acid than H_2SO_4.

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