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Proton-Donating Power of 100% Perchloric Acid: An MP2 Study

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Abstract—The ab initio quantum chemical method MP2 with a 6-311++G(*d*, *p*) basis set is used to calculate the energy of gas-phase solvation of the $H_2ClO_4^+$ cation and ClO_4^- anion by one perchloric acid molecule. The energy of additional solvation of the resulting complexes by liquid perchloric acid is estimated within the continuum model of solvation by the PCM method, with the acid modeled as a continuum with a large dielectric constant of $\varepsilon = 115$. The calculated data have provided an almost quantitative estimate for the energy of self-ionization of 100% liquid perchloric acid. The similarly calculated energy of solvation of protons by 100% perchloric acid is 30.7 kcal/mol lower than the heat of hydration of protons in aqueous solution. This result explains the fact that anhydrous perchloric acid exhibits the properties of a superacid.

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Researchers' attention is being increasingly attracted by acid catalysts, among which perchloric acid and its derivatives occupy an important place. Perchloric acid is the strongest of the mineral acids. Its oxidizing activity increases sharply as its concentration approaches 100% [1]. Undiluted $HClO_4$ instantly ignites all oxidizable organic compounds and vigorously oxidizes almost all metals. Anhydrous $HClO_4$ is a volatile compound. It is unstable at room temperature and turns yellow because of the formation of lower chlorine oxides. Perchloric acid cannot be distilled at atmospheric pressure because of its decomposition. However, perchloric acid distillation at a reduced pressure yields a distillate consisting of $HClO_4$ and Cl_2O_7 [2]. Anhydrous $HClO_4$ is a strong proton donor. Perchloric acid in aqueous solution is the strongest among the known acids [3]. The dissociation constant of 100% perchloric acid is as small as 10^{-8} [4]. Dilution of 100% perchloric acid with water significantly increases its degree of ionization, but it reduces its strength in terms of the Hammett acidity function H_0 [5]. Anhydrous $HClO_4$ can be viewed as a superacid, for it is capable of protonating even very weak bases [6, 7]. Note that, when mixed with various acids, perchloric acid participates in the formation of acido salts not as a proton acceptor, but as a proton donor. Perchloric acid is widely used both in the industry and in the laboratory as, e.g., a catalyst for hydrolysis, etherification, and various rearrangements in organic compounds [8].

Earlier [9], we hypothesized that the major factor determining the proton-donating power of superacids is the low energy of proton solvation by superacid molecules rather than the dissociation constant of the acid. Here, we use ab initio quantum chemical calculations to evaluate solvation processes in 100% perchloric acid and to analyze the energy balance of the self-ionization of the acid, taking into account the solvation effects. We used this theoretical approach in earlier works to investigate reactions of carbenium ions in acid media [10, 11] and to study the autoprotolysis of strong acids [12, 13].

COMPUTATIONAL PROCEDURE

Calculations for molecular systems in their ground state were performed by the second-order Möller–Plesset perturbation theory method (MP2) using a 6-311++G(*d*, *p*) basis set [14, 15]. Full geometry optimization was carried out for all molecular systems and complexes examined. The enthalpies of molecular systems at $T = 298.15$ K were precisely calculated by the composite method CBS-QB3 [16, 17]. The solvent effect on the complexation energy was estimated using the continuum model PCM [18, 19] and the geometric parameters determined by the MP2(full)/6-311++G(*d*, *p*) method taking into account the core electrons. In the calculation of the energy of proton solvation by perchloric acid, we used the proton affinity of the $HClO_4$ molecule in the gas phase that was precisely calculated by the CBS-QB3 method (+149.62 kcal/mol) and the energy of solvation of the $H_2ClO_4^+$ ion calculated by the PCM method. The solvation energy was calculated in two steps. Initially, we calculated the structure and energy of formation of the $(H_2ClO_4 \cdot HClO_4)^+$ ion in the gas phase in the cluster approximation with full geometry optimization, applying a vibration energy correction. Next, in the framework of the continuum model of solvation, using the PCM method, we estimated the additional contribution from the electrostatic interaction of the

Results of the MP2(full)/6-311++G(*d*, *p*) calculations: total energies (*E*(MP2)), zero-point energies (*E*(ZPE)), and thermal contributions to the enthalpy ($\Delta H(T)$) at $T = 298$ K for the $HClO_4$ molecule, $H_2ClO_4^+$ and ClO_4^- anions, and complexes of $H_2ClO_4^+$ and ClO_4^- with perchloric acid in the gas phase

Molecular species	*E*(MP2), a.u.	*E*(MP2) + *E*(ZPE), a.u.	*E*(MP2) + *E*(ZPE) + Δ*H*(*T*), a.u.	*E*(PCM), kcal/mol
$HClO_4$	−760.281005	−759.773174	−759.768224	–
$H_2ClO_4^+$	−760.535788	−760.497603	−760.491469	–
ClO_4^-	−759.788800	−759.773174	−759.768224	–
$(H_2ClO_4HClO_4)^+$	−1520.849926	−1520.782806	−1520.770791	68.52
$(ClO_4\,HClO_4)^-$	−1520.114028	−1520.070995	−1520.059950	51.81

$(H_2ClO_4 \cdot HClO_4)^+$ ions with the surrounding perchloric acid molecules to the solvation energy. Here, perchloric acid was modeled as a continuous medium with a dielectric constant of $\varepsilon = 115$ [3]. In order to verify the reliability of the results thus obtained, we calculated the energy of solvation of the ClO_4^- anion. The calculated value was then used to estimate the energy of self-ionization of liquid perchloric acid, and this value was compared with the experimental value of the heat of self-ionization (11.2 kcal/mol) [4]. The calculated values of the total energies (***E*(MP2)**) of $HClO_4$, $H_2ClO_4^+$, and ClO_4^- and of the energies of interaction of the $H_2ClO_4^+$ cation and ClO_4^- anion with perchloric acid in the gas phase are listed in the table. Zero-point energies (***E*(ZPE)**) and thermal contributions to the enthalpy (**Δ*H*(*T*)**) for the $HClO_4$ molecule, $H_2ClO_4^+$ and ClO_4^- ions, and $(H_2ClO_4 \cdot HClO_4)^+$ and $(ClO_4 \cdot HClO_4)^-$ complexes are also included in the table. The quantum chemical calculations were carried out using the Gaussian-03 program [20] on a Linux-powered PC cluster.

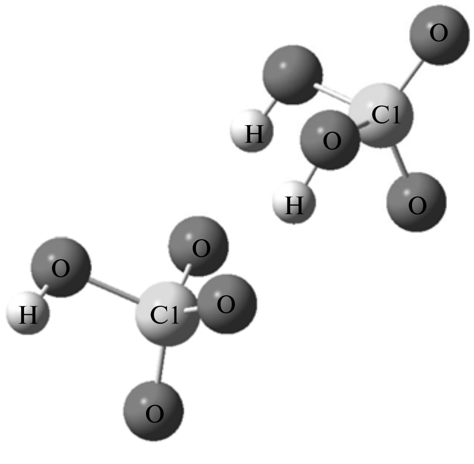

Fig. 1. MP2/6-311++G(*d*, *p*)-optimized structure of the $(H_2ClO_4 \cdot HClO_4)^+$ complex.

RESULTS AND DISCUSSION

The results of our calculations demonstrated that the most stable structure of the $(H_2ClO_4 \cdot HClO_4)^+$ complex is the one that has two almost equivalent short hydrogen bonds linking the two OH groups of the $H_2ClO_4^+$ cation to oxygen atoms of $HClO_4$ (1.722 and 1.759 Å, Fig. 1). The energy of formation of this complex in the gas phase, with the vibration correction taken into account, is 19.48 kcal/mol. The contribution from the additional electrostatic interaction with the surrounding perchloric acid molecules to the solvation energy, estimated using the continuum model, further raises the solvation energy by 68.52 kcal/mol (table). In order to determine the total energy of solvation of the cation of liquid perchloric acid, we subtracted, from the calculated solvation energy, a correction for the passage of one molecule of 100% perchloric acid into the gas phase. This correction can be taken to be equal to the experimental heat of evaporation of 100% perchloric acid, which is 7.35 kcal/mol [3]. Thus, the total energy of solvation of the $(H_2ClO_4 \cdot HClO_4)^+$ ion by liquid perchloric acid is 80.65 kcal/mol. The liquid perchloric acid affinity of the proton can now be derived from the following thermodynamic cycle:

$$HClO_{4g} + H^+ \rightarrow H_2ClO_{4g}^+ \quad -149.62 \text{ kcal/mol},$$

$$HClO_{4l} \rightarrow HClO_{4g} \quad +7.35 \text{ kcal/mol},$$

$$H_2ClO_{4g}^+ + HClO_{4g} \rightarrow (H_2ClO_4 \cdot HClO_4)_g^+ \quad -19.48 \text{ kcal/mol},$$

$$(H_2ClO_4 \cdot HClO_4)_g^+ + HClO_{4l} \rightarrow H_2ClO_{4l}^+ \quad -68.52 \text{ kcal/mol},$$

$$H_2ClO_{4g}^+ + HClO_{4l} \rightarrow H_2ClO_{4l}^+ \quad -230.27 \text{ kcal/mol}.$$

This yields an affinity value of 30.7 kcal/mol, which is smaller than the heat of hydration of the proton in aqueous solution (261 kcal/mol) [7].

To check the accuracy of our quantum chemical calculations, we calculated the energy of self-ionization of liquid perchloric acid, which was then compared to the experimental heat of self-ionization (11.2 kcal/mol) [4]. For this purpose, using the same scheme as in the case of the $H_2ClO_4^+$ cation, we initially determined the energy of the interaction between the ClO_4^- anion and one perchloric acid molecule in the gas phase; next, using the continuum model, we estimated the contribution from the additional interaction of the $(ClO_4 \cdot HClO_4)^-$ anions with the surrounding molecules of liquid perchloric acid to the total solvation energy. The structure of the most stable complex, $(ClO_4 \cdot HClO_4)^-$, which results from the interaction between the ClO_4^- anion and one perchloric acid molecule, is shown in Fig. 2. The bonding between the ClO_4^- anion and the perchloric acid molecule is due to a short hydrogen bond (1.397 Å). According to our calculations, the energy of solvation of the ClO_4^- anion by one perchloric acid molecule in the gas phase is –27.26 kcal/mol, which is 7.78 kcal/mol higher than the same energy for the $H_2ClO_4^+$ cation. As calculated within the continuum model, the additional contribution from the electrostatic interaction of the $(ClO_4 \cdot HClO_4)^-$ ions with liquid perchloric acid to the total energy of solvation of these ions is –51.81 kcal/mol (table). Thus, with the correction for the dissociation energy of one hydrogen bond in liquid perchloric acid taken into account, the total energy of solvation of the ClO_4^- anion is –71.72 kcal/mol.

To estimate the self-ionization energy of liquid perchloric acid, we will use the calculated self-ionization energy of perchloric acid in the gas phase, which is 148.64 kcal/mol. With the calculated energies of solvation of the $H_2ClO_4^+$ cation and ClO_4^- anion taken into account, the energy balance for the self-ionization of liquid perchloric acid appears as follows:

$$2HClO_{4l} \rightarrow 2HClO_{4g} + 14.70 \text{ kcal/mol},$$

$$2HClO_{4g} \rightarrow H_2ClO_{4g}^+ + ClO_{4g}^- + 148.64 \text{ kcal/mol},$$

$$H_2ClO_{4g}^+ + HClO_{4l} \rightarrow H_2ClO_{4l}^+ - 80.65 \text{ kcal/mol},$$

$$ClO_{4g}^- + HClO_{4l} \rightarrow ClO_{4l}^- - 71.72 \text{ kcal/mol},$$

$$2HClO_{4l} \rightarrow H_2ClO_{4l}^+ + ClO_{4l}^- + 10.97 \text{ kcal/mol}.$$

The coincidence between the calculated and experimental values of the heat of self-ionization is nearly quantitative, which is convincing evidence that our calculations are satisfactorily accurate.

In the earlier literature [21, 22], it was noted that protons in anhydrous perchloric acid are anomalously reactive. Our numerical data provide a quite natural explanation for this fact: the heat of solvation of protons in 100% perchloric acid is 30.7 kcal/mol lower than in aqueous solution, and it is this circumstance that makes the protons more reactive. This conclusion seems quite natural in view of the fact that superacids obviously solvate protons less strongly than molecules of water, a more basic compound. Superacids ensure a favorable balance between the weaker solvation of protons and the fairly high total heat of solvation of protons and anions owing to which the heterolytic dissociation of the acids is satisfactorily extensive. This effect is due to the fact that, as compared to aqueous solutions, the superacid solvates the anions more strongly. For example, according to our calculations, the energy of solvation of the perchlorate anion by one perchloric acid molecule is 27.3 kcal/mol, approximately 16 kcal/mol higher than the energy of hydration of this anion by one H_2O molecule.

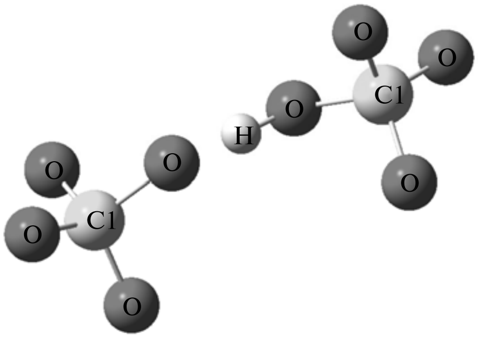

Fig. 2. MP2/6-311++G(*d*, *p*)-optimized structure of the $(ClO_4 \cdot HClO_4)^-$ complex.

Thus, for superacids, the ionization constant is not the determining factor, and their strength is determined by the anomalously high reactivity of the protons, which is due to the low energy of their solvation.

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