Intracluster Proton Transfer

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Critical Size for Intracluster Proton Transfer from Water to an Anion**

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Proton transfer (PT) is a fundamental process in solution chemistry and in biology and has been the subject of numerous studies.[1,2] In the past several decades, studies of proton transfer have been pursued in the gas phase to understand the nature of acidity in small microscopic systems and nanometric confined geometries.[3] Kebarle and co-workers have pioneered these studies using high-pressure mass spectrometry (HPMS).[4,5] By measuring the relative concentrations of protonated donor and acceptor species at controlled conditions of temperature and pressure, the relative enthalpies, entropies, and free energies of a wide range of molecules and clusters were determined. Most subsequent studies relied on mass spectrometry (ion cyclotron resonance (ICR)[3] and flow tube reactors).[6] All of these studies explored the equilibrium of separate species in the gas phase and did not monitor the equilibrium between the proton donors and acceptors in the same microenvironment. The first experiments on intracluster PT in the gas phase explored photoinduced processes. Cheshnovsky and Leutwyler[7] observed excited-state proton transfer (ESPT) in α-naphthol solvated in ammonia clusters.[8] In these experiments, spectroscopic methods (resonance two-photon ionization and dispersed fluorescence) were used. Similar experiments on phenol[9] followed, and the ultrafast dynamics of ESPT were explored,[10,11] accompanied by ab initio calculations and simulations.[12,13] Despite the general acceptance of the phenomenon of ESPT in clusters, the interpretation of several findings remains controversial. Some researchers discuss the experimental findings in terms of H-atom transfer and electronic-ground-state PT.[14,15]

The mechanisms of photoinduced and ground-state PT may differ greatly, hence the importance of understanding the latter processes. Bowen and co-workers[16] have shown that barrier-free PT from a complexing alcohol molecule to a nucleic acid anion in the ground state can be observed by monitoring the results of photoelectron spectroscopy (PES) of the complexes. In these systems, PT is governed by the acidity of the alcohol. Johnson and co-workers used IR spectroscopy to monitor proton transfer in the ground state of protonated dimer clusters.[17]

Herein, we report on the first direct observation (by PES) of a critical cluster size for intracluster PT in the ground state. We show that beyond a critical number of solvent water molecules in clusters $(C_6H_5NH^-)\cdot(H_2O)_n$, one water solvent molecule turns more acidic than the corresponding solvated anion, and donates its proton to form solvated hydroxy clusters of the nature $(C_6H_5NH_2)\cdot(OH^-)\cdot(H_2O)_{n-1}$. Essentially, we observe the change in the relative ground-state acidity of two molecules, water and aniline, induced by the extent of solvation.

The systems studied are negatively charged, proton-deficient systems and as such are analogous to a basic environment in which the bases compete for protons and the solvation energetics of the corresponding anions affect the equilibrium states.

Examination of the PE spectra of clusters matching the masses of $(C_6H_5NH^-)\cdot(H_2O)_n$ (Figure 1) reveals two distinct regimes. The spectra of clusters corresponding to $n = 1,2$ are similar to the spectra of the bare deprotonated aniline (DPA)

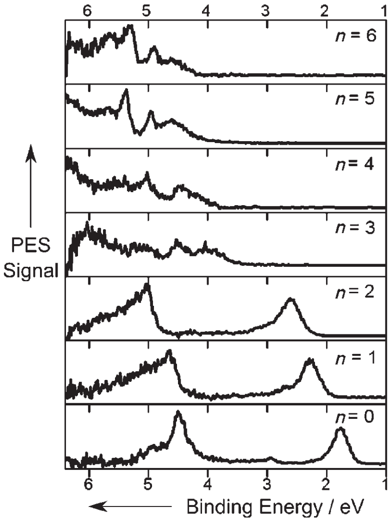

Figure 1. Photoelectron spectra of $(C_6H_5NH^-)\cdot(H_2O)_n$ or $(C_6H_5NH_2)\cdot(OH^-)\cdot(H_2O)_{n-1}$, $n = 0$–6.

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but shifted to higher binding energy (BE) by approximately 0.5 eV per water molecule, as can be anticipated in the spectra of anions solvated in polar-molecule clusters.[18] The spectra corresponding to $n>2$ water molecules look considerably different. The two distinct peaks of water-solvated DPA are replaced by broad structures which we attribute to OH^- solvated in neutral molecular aniline and water molecules. The remarkable change in the PE spectra is induced by PT from water to DPA in the ground state of the cluster. This interpretation is supported by the similarity of the new spectral features to those of $OH^-(H_2O)_n$ $n=1,2$ observed by the groups of Neumark[19] and Continieti.[20,21]

Ab initio calculations were carried out to allow a better understanding of the experimental findings. Global and local minimum structures of the aqueous DPA clusters are shown in Figure 2. For $n=1,2$, the minimum-energy structures correspond to $(C_6H_5NH^-)\cdot(H_2O)_n$, with excess negative charge localized at the nitrogen atom of DPA. Local minima corresponding to $(C_6H_5NH_2)\cdot(OH^-)\cdot(H_2O)_{n-1}$, namely a solvated hydroxy anion, were not found for $n=1$ or 2, although an extensive search for such minima was made. It seems safe to conclude that these species do not exist.

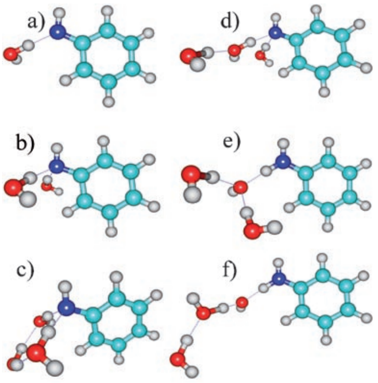

Figure 2. Computed global (a, b, e for $n=1$–3, respectively) and local (c, d, f for $n=3$) minima of $(C_6H_5NH^-)\cdot(H_2O)_n$ or $(C_6H_5NH_2)\cdot(OH^-)\cdot(H_2O)_{n-1}$, $n=1$–3. See text for details.

The BE of the electrons in the anions were computed by CIS (configuration–interaction singles) methods for $n=1,2$, and the results were compared directly with the experimental peak positions. For both $n=1$ and $n=2$, the shift in the PE peak to higher BE per water molecule is about 0.5 eV. In the calculations for $n=1$ the shift is 0.52 eV and for $n=2$ the shift is 0.50 eV. Thus, the agreement between the computed and the experimental electron BE is very good. The bond strength of a single water molecule to $C_6H_5NH^-$, including the zero-point energy, is 0.63 eV. Clearly, the final neutral state $(C_6H_5NH)\cdot(H_2O)$ generated in the vertical photoelectron detachment contributes significantly to the resulting electron binding energy of 0.50 eV.

The computational results, in accord with the experiment, are dramatically different for clusters containing three water molecules. Several minima are obtained in the calculations of clusters containing three water molecules (Figure 2 c–f). The global minimum corresponds to a solvated hydroxy ion: $(C_6H_5NH_2)\cdot(OH^-)\cdot(H_2O)_2$ (Figure 2 e). The energies of the other structures relative to the global minimum are 0.10, 0.16, and 0.26 eV for structures in Figure 2 f, c, d, respectively. Proton transfer at this cluster size is expressed in specific changes in N–H and O–H distances in the computational results.

Of the two shortest N–H separations in the calculations, one (ca. 1.03 Å) remains essentially constant for all cluster sizes and structures. This is clearly a covalent N–H bond. The other N–H separation changes from about 1.70 Å in Figures 2 a–d to 1.07 Å in the global minimum configuration of $(C_6H_5NH_2)\cdot(OH^-)\cdot(H_2O)_2$ (Figure 2 e). The larger distance represents hydrogen bonding, while the 1.07-Å length indicates covalent N–H bonding, which is slightly stretched by hydrogen bonding to the OH^- ion. The same manifestation of proton capture by DPA is revealed by monitoring the two shortest O–H separations, one of which changes from about 1.0 to 1.57 Å with the addition of the third water molecule to the cluster. More calculated data are given in the Supporting Information.[22]

While $(C_6H_5NH_2)\cdot(OH^-)\cdot(H_2O)_2$ is the most stable species of this mass, the species $(C_6H_5NH^-)\cdot(H_2O)_3$ is predicted to be stable in a local minimum of the potential energy surface. It is doubtful whether $(C_6H_5NH^-)\cdot(H_2O)_3$ can be observed in the present experimental conditions, as the energy difference between the two clusters is relatively large (above 0.16 eV). However, the computations suggest the possibility of observing the hydrated DPA species and a PT process induced by vibrational excitation of $(C_6H_5NH_2)\cdot(OH^-)\cdot(H_2O)_2$.

It seems that the underlying driving force for the change in acidity of the two components (aniline and water) is the relative stabilization of the ionic conjugate base. Despite the fact that isolated aniline is a stronger acid than H_2O,[23] the hydroxy anion is better solvated in the water cluster owing to its smaller size. Indeed, in bulk water solution H_2O is a much stronger acid than aniline, and the equilibrium constant for the reaction in Equation (1) is $K=2.9\times10^{-12}$ based on the corresponding pK_a of water (15.7) and aniline (27.3) in aqueous solution.[24]

$$C_6H_5NH_2 + OH^- \rightleftharpoons C_6H_5NH^- + H_2O \quad (1)$$

To conclude, this is the first time in which the relative change of acidity of two constituents has been observed in ground-state clusters. This phenomenon may be important in the restricted geometry of proteins and other biological systems in which the number of solvent molecules is limited.

Experimental Section

A detailed description of our experimental setup can be found elsewhere.[18] A wide distribution of clusters is generated with a 10-Hz pulsed nozzle (Even–Lavie valve).[25] Argon at 4–6 bar is passed into the valve through a heated (70 to 100 °C) reservoir containing aniline and water. The supersonic expansion is intersected by an electron beam (ca. 200 eV) generating a distribution of negatively charged clusters. A three-zone Willy–McLaren[26] time-of-flight (TOF) mass spectrometer ($m/\Delta m\approx300$) is used for mass analysis. The clusters matching the masses of $(C_6H_5NH^-)\cdot(H_2O)_n$, $n=0$–8, were generated and mass selected before entering a magnetic-bottle TOF photoelectron spectrometer.[27,28]

Typical estimated temperatures of the clusters, based on their ability to bind argon atoms, were a few tens of Kelvin. PE spectra were recorded with 5-ns, 193-nm photons from a narrow-band ArF excimer laser.[29]

Computational methods: Ab initio calculations at the MP2/DZP level were carried out on the experimentally studied clusters. The general atomic and molecular electronic structure system GAMESS[30] was used for these calculations. The global and local minima structures of the aqueous DPA clusters are shown in Figure 2. Comparison of the DZP results with calculations for the higher-level TZP in the case of DPA showed very close agreement. The percentage of deviation of the bond lengths from the high level TZP is only 0.4% and of the angles it is 7.3%.These results give confidence in using DZP in this case.

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