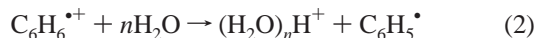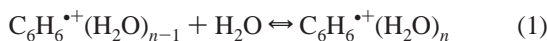# Stepwise Hydration and Multibody Deprotonation with Steep Negative Temperature Dependence in the Benzene•+−Water System

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Hydrogen bonding and hydrophobic interactions play central roles in many processes that involve the hydration of aliphatic and aromatic hydrocarbons and their ions.[1,2] The benzene•+ cation (Bz•+)−water system provides a prototype of hydrophobic hydration at macroscopic scales.[2−4] In this contribution, we provide the first study of the gas-phase hydration of Bz•+ and the thermochemistry of hydration by 1−8 water molecules. We also present the first report of the deprotonation of an aromatic ion by water molecules and the first temperature study of a multibody process that requires the bonding of five components (Bz•+ + 4H₂O), resulting in an unprecedented large negative temperature coefficient ($k = CT^{-67 \pm 4}$ or $E_a = -34 \pm 1$ kcal mol⁻¹).

The thermochemical and kinetics data were obtained using mass-selected drift cell experiments as described in detail elsewhere.[5] Mass-selected benzene ions (Bz•+), formed by EI, were injected at low energy into a drift cell containing H₂O vapor at 0.1−0.3 Torr, at controlled temperatures from 233 to 350 K. The thermalized ions traveled through the drift cell under a uniform electric field of 1.5−3 V/cm. Ions exiting the cell were collected and yielded arrival time distributions (ATDs). For the stepwise hydration reactions (1) the ion intensity ratio Bz•+(H₂O)$_n$/ Bz•+(H₂O)$_{n-1}$ was measured from the integrated peak areas of the ATDs as a function of decreasing cell drift field corresponding to increasing reaction time. Typically, rapid equilibrium was obtained in the association reactions (1), while the time studies showed slow deprotonation of Bz•+ with decrease of the Bz•+(H₂O)$_n$ clusters and formation of (H₂O)$_n$H⁺ clusters in the overall reaction (2). Other ion−molecule reactions producing protontated water clusters have been studied previously.[6]

$$C_6H_6^{\bullet+}(H_2O)_{n-1} + H_2O \Leftrightarrow C_6H_6^{\bullet+}(H_2O)_n \qquad (1)$$

$$C_6H_6^{\bullet+} + nH_2O \rightarrow (H_2O)_nH^+ + C_6H_5^{\bullet} \qquad (2)$$

Equilibrium was evidenced by the identical ATDs of the Bz•+(H₂O)$_{n-1}$ and Bz•+(H₂O)$_n$ ions, and it was also confirmed by the constancy of the equilibrium constants with varying $P(H_2O)$ and total pressure ($P(H_2O) + P(He)$). The resulting van't Hoff plots yielded $\Delta H_{n-1,n}^{\circ}$ and $\Delta S_{n-1,n}^{\circ}$ as shown in Table 1.

Figure 1 displays product ion distributions after the injection of Bz•+ into 0.12 Torr H₂O vapor at 239 K. Two main groups of ions are observed: hydrated benzene ions BW$_n$ ($n = 1-8$) and protonated water clusters H⁺W$_n$ ($n = 4-8$) formed by the deprotonation reactions (2). However, only a small concentration of Bz•+(H₂O)₃, BW₃, was observed under any conditions. This is due to the stepwise deprotonation reaction (3), which becomes thermoneutral or exothermic (within the accuracy of the literature data) in the $n = 4$ step (Table 1) and depletes the C₆H₆•+(H₂O)₃ ion. For this reason, the very small concentration of the Bz•+(H₂O)₃ cluster prevented a reliable measurement of the equilibrium between C₆H₆•+(H₂O)₂ and C₆H₆•+(H₂O)₃ clusters under the current experimental conditions.

$$C_6H_6^{\bullet+}(H_2O)_{n-1} + H_2O \rightarrow (H_2O)_nH^+ + C_6H_5^{\bullet} \qquad (3)$$
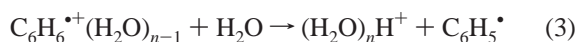
Table 1. Thermochemistry of Clustering Reactions (1) and of Proton Transfer Reactions (2) and (3)

|	clustering equilibrium (1)		proton transfer reaction (2)	proton transfer reaction (3)
n	$\Delta H_{n-1,n}^{\circ\ a}$	$\Delta S_{n-1,n}^{\circ\ a}$	$\Delta H_n^{\circ a,b}$	$\Delta H_n^{\circ a,b}$
1	−9.0	−19.5	46	46
2	−8.0	−18.9	14	23
3	(−8)^c		−7	10
4	−10.3	−22.4	−25	0
5	−8.6	−18.1	−38	−3
6	−7.8	−15.1	−49	−5
7	−9.8	−25.5	−60	−8
8	−11.1	−32.6	−70	−9

^{a} Units: ΔH° in kcal mol⁻¹, ΔS° in cal mol⁻¹ K⁻¹. Error estimates based on standard deviations of van't Hoff plots, $\Delta H^{\circ} \pm 1.5$ kcal mol⁻¹, $\Delta S^{\circ} \pm 4$ cal mol⁻¹ K⁻¹. ^{b} Calculated based on data in NIST compilation (cumulative uncertainty of terms in eqs 2 and 3 estimated as ± 3 kcal mol⁻¹).[11] ^{c} Estimated based on $n = 2$ value.
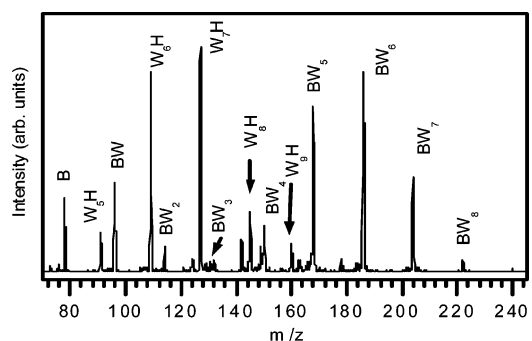
Figure 1. Mass spectrum obtained after injecting C₆H₆•+ into H₂O vapor (0.12 Torr at 239 K) in the ion mobility cell. Note the formation of hydrated Bz•+(H₂O)$_n$ (i.e., BW$_n$) and the deprotonation products H⁺(H₂O)$_n$ (i.e., W$_n$H).

In accord, the ATDs of the hydrated benzene ions were also divided into two groups (see Supporting Information). The ATDs of the Bz•+(H₂O)$_n$ ($n = 0-2$) were equal, showing that they were in equilibrium, and the ATDs of the larger clusters ($n = 3-8$) were equal to each other but slightly shifted from the first group.

The measured thermochemical values, shown in Table 1, are unusual in that the binding energies change little from $n - 1, n = 0,1$ to 7,8, unlike the usual regular decrease with n.[7] Our preliminary ab initio (ROHF/6-31+G**)[8] calculations confirmed this trend and showed that it can be attributed to 99−96% of the charge in the $n = 1-3$ clusters remaining on the Bz•+ core ion. In the minimum energy structures of the Bz•+(H₂O)$_n$ clusters ($n = 1-3$), the first solvent water molecule is attached to Bz•+ with a CH⁺···OH₂ bond, in agreement with previous calculations.[4] The additional water molecules are hydrogen-bonded to the first water molecule. The solvent starts to form effectively neutral water clusters, but being attached to Bz•+ (or to C₆H₅• through H⁺) allows studying their structures by mass spectrometry. For example, the measured $-\Delta G_{4,5}^{\circ}$ exhibits the largest values among the measured equilibria over a temperature range of 240−275 K (see Supporting Information). This
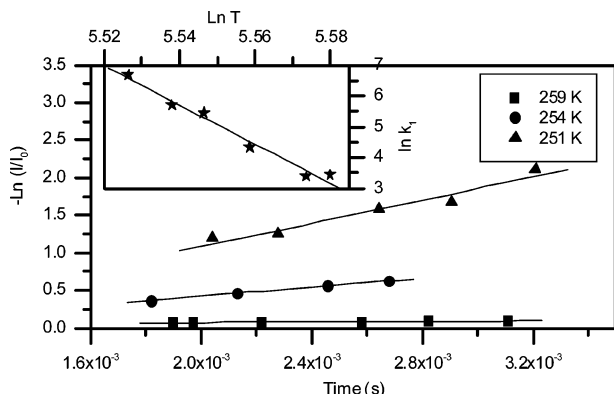
Figure 2. Kinetic plots for the change of ion intensities ($-\ln I/I_0$) versus reaction time [$I = \Sigma I(\text{Bz}^{\bullet+}(\text{H}_2\text{O})_n)$, $I_0 = \Sigma I(\text{Bz}^{\bullet+}(\text{H}_2\text{O})_n + \text{H}^+(\text{H}_2\text{O})_n)$]. The inset shows the change of first-order rate constant versus temperature.

may reflect the formation of a cyclic water cluster which is the lowest energy structure of the neutral water pentamer.[9] This and the drop in the $-\Delta S_{5,6}^\circ$ value indicate the closing of a solvent shell.[7] Also, a remarkable increase in the $-\Delta S_{6,7}^\circ$ and $-\Delta S_{7,8}^\circ$ values indicates strong orientational restraint of water in these larger clusters.[9] In fact, three-dimensional cagelike structures consisting of seven- and eight-member rings are the lowest energy conformers of the water heptamer and octamer.[9,10] The observed large negative entropy of the $\text{Bz}^{\bullet+}(\text{H}_2\text{O})_8$ cluster may be consistent with the formation of a cagelike structure by eight H_2O molecules similar to neutral water clusters.[9,10]

An alternative structure of the stable $\text{Bz}^{\bullet+}(\text{H}_2\text{O})_n$ clusters would be formed by internal proton transfer to form $(\text{H}_2\text{O})_n\text{H}^+$ bonded to the $\text{C}_6\text{H}_5^\bullet$ radical (see Supporting Information). We tested for this possibility by injecting $\text{C}_6\text{H}_6^{\bullet+}$ into D_2O vapor. If $\text{C}_6\text{H}_5^\bullet(\text{D}_2\text{O})_n\text{H}^+$ formed, the $(\text{D}_2\text{O})_n\text{H}^+$ moiety within the hydrated clusters should exchange the H^+ to form $\text{C}_6\text{H}_5^\bullet(\text{D}_2\text{O})_n\text{D}^+$ clusters. This did not occur for any of the $n = 1-8$ clusters, confirming that $\text{C}_6\text{H}_6^{\bullet+}$ (or $\text{C}_6\text{H}_5^\bullet\cdots\text{H}^+$) remains the core ion in the stable clusters under our conditions.

However, the internal proton transfer may take place in the activated complexes of reaction (3) when the next H_2O molecule attaches to the $(n-1)$-th cluster to form an excited $[\text{C}_6\text{H}_6^{\bullet+}(\text{H}_2\text{O})_n]^*$ complex. Our preliminary ab initio calculations indicated that the internal proton transfer $[\text{C}_6\text{H}_6^{\bullet+}(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5^\bullet(\text{H}_2\text{O})_n\text{H}^+]$ is slightly endothermic at the SCF level for $n = 4$ (exothermic in the higher steps), so that the 10 kcal mol^{-1} binding energy released into the complex on adding the fourth H_2O molecule can result in dissociative proton transfer that forms the observed $(\text{H}_2\text{O})_n\text{H}^+$ products. The need for the internal excitation energy was confirmed by pressure studies where adding $0.25-1.5$ Torr helium to the water vapor in the drift cell quenched the reaction, and the protonated water clusters became negligible.

The overall process converts the equilibrium-coupled $\text{C}_6\text{H}_6^{\bullet+}(\text{H}_2\text{O})_n$ ions to the equilibrium-coupled $(\text{H}_2\text{O})_n\text{H}^+$ clusters, resulting in the decay of the $\text{C}_6\text{H}_6^{\bullet+}(\text{H}_2\text{O})_n$ ions in parallel with each other and the compensating increase of the $(\text{H}_2\text{O})_n\text{H}^+$ ions. We performed time-resolved kinetic measurements at several temperatures as shown in Figure 2. The rate constants showed steep negative temperature dependence. For example, the first-order rate coefficient (k_f) increased by a factor of 26, from 31 to 797 s^{-1} over a range of only 14°, from 251 to 265 K (higher order rate coefficients changed equally).[12]

The negative temperature coefficients may be expressed as $k = AT^{-n}$, with $n = 2$ to 8 reported, or as Arrhenius plots of ln k vs $1/T$, where the temperature dependences are expressed as negative activation energies.[13] Here, the rates of the conversion of the

equilibrium-coupled $\Sigma\text{Bz}^{\bullet+}(\text{H}_2\text{O})_n$ ions into $\Sigma(\text{H}_2\text{O})_n\text{H}^+$ ions show a uniquely large negative temperature coefficient of $k = AT^{-67} \pm 4$ or an activation energy of -34 ± 1 kcal mol^{-1}.

The unusual temperature coefficient can be assigned to the multibody nature of the reaction. As noted above, the stepwise reaction (3) that applies here is exothermic for $n \geq 4$, and the enthalpy for converting the injected $\text{Bz}^{\bullet+}$ ion to this reactive fraction (i.e., $\Sigma\Delta H_{n-1,n}^\circ$ ($n = 1-4$)) for $\text{Bz}^{\bullet+} \rightarrow \text{Bz}^{\bullet+}(\text{H}_2\text{O})_4$ is -35 kcal mol^{-1} (Table 1). This is similar to the observed negative Arrhenius activation energy, suggesting that assembling the reactive entity is the controlling factor. This appears to be the first temperature study of reactions where more than two reactants are assembled in the gas phase. Large negative temperature effects should be general for such multibody processes.

In summary, we observed the thermochemistry of the initial steps in the hydrophobic hydration of the ionized hydrocarbon ion $\text{C}_6\text{H}_6^{\bullet+}$. We found experimental and theoretical evidence for effectively neutral water clusters hydrogen-bonded to the aromatic ion and thermochemical evidence for the formation of cyclic and cagelike structures in these neutral-like clusters. We also observed the multibody deprotonation of the ion where several components (here $(\text{H}_2\text{O})_n$) need to be assembled from the gas phase to form a reactive entity. The resulting unprecedented steep temperature coefficient should be a general property of such stepwise-assembled multicomponent reactions.

We are conducting ab initio and molecular mechanics calculations and observing other solvated aromatic ion systems with different energetics to understand these reaction mechanisms and their temperature effects in more detail.

Supporting Information Available: Figures of the ATDs of $\text{C}_6\text{H}_6^{\bullet+}(\text{H}_2\text{O})_n$, $n = 0-5$ and $\Delta G^\circ(T)$ for $\text{C}_6\text{H}_6^{\bullet+}(\text{H}_2\text{O})_n$, $n = 1-7$. This material is available free of charge via the Internet at http://pubs.acs.org.

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