Chemistry of Aromatic Cations on Water Clusters: Magic Numbers as a Mass Spectroscopic Diagnosis of Reactivity

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The chemical reactivity of benzene cations in medium-sized ($n \sim 25$) $(H_2O)_n$ water clusters has been investigated. After formation in a supersonic jet, the neutral Bz-$(H_2O)_n$ species are ionized by resonance-enhanced two-photon ionization. The existence of magic numbers in the mass spectra of these cluster ions has been revealed by reflectron time-of-flight mass spectrometry. These magic numbers are assigned to size-dependent evaporation processes following the ionization. The similarities observed for the present magic numbers compared to those of protonated water clusters allow us to assign them to the formation of a protonated water cluster without ejection of the benzenoid product from the cluster ion. With this diagnosis, we present evidence for the existence of a size-dependent chemical reactivity of benzene cations: a reaction is observed in the medium size range ($n \sim 20-30$), whereas small clusters are known not to react. This result is compared to the chemical reactivity of toluene$^+$ in water clusters as well as to experimental data concerning liquid phase reactions.

1. Introduction

The study of chemical reactions in clusters has recently become of growing interest to the scientific community.[1−6] In particular, the chemical properties of aromatic cations in small solvent clusters have been studied using this new approach, which is especially suited to investigate size effects of the solvating environment.[7−9] Cluster experiments provide several advantages: on one hand, laser ionization of neutral clusters, using resonance-enhanced multiphoton ionization techniques, offers an efficient way to form solvated cations, without using strong chemical oxidants like in liquid phase studies,[10−13] and it allows the experimentalist to control the cluster size by the means of size-selective spectroscopy. On the other hand, proton transfer reactions from the ion to surrounding solvent molecules can be easily monitored by standard mass spectroscopic techniques, if the exothermicity of the reaction is large enough to separate the reaction products and to give rise to nascent protonated solvent clusters, which is known to be the case at least in small clusters.[7−9] Finally, the cluster confinement provides the possibility to stabilize and isolate the primary reaction products, thus suppressing secondary reactions.

The aromatic cations are already known for their high reactivity in aqueous solutions.[10−15] Cations can be formed only under very strong oxidizing conditions or using pulsed radiolysis, and they are characterized either by a strong acidity, leading to a neutral aromatic radical, or by their ability to react with a water molecule and to give rise to a neutral OH adduct.[11−13] In both cases the balance of the chemical reaction results in the liberation of a proton. For instance, toluene (To) cations are known to give both products in neutral aqueous solution,[12] whereas benzene (Bz) cations only lead to the formation of the OH adduct.[12,14]

Two groups have investigated the acidity of To cations in To$^+$−S$_n$ clusters (S = water, methanol, ethanol) using lasers combined with mass spectrometry.[7−9] The main question addressed by these authors concerns the possible existence of a critical cluster size for the proton transfer to take place, which is suggested by the size-dependent proton affinity (Table 1) of water clusters.[16] These experiments showed that three water molecules are necessary to deprotonate toluene$^+$, thereby ejecting a benzyl radical from the cluster (unobserved) and forming a small protonated water cluster that has been detected by mass spectrometry.[8,9] The observation of the reaction in the small clusters is in fair agreement with the proton affinity of water clusters (Table 1), which suggests that the reaction is energetically accessible for $n \geq 3$, if one neglects the effects of solvation.

TABLE 1: Energetic Data (in kcal/mol) Pertinent for the Discussion of Reactivity of the Benzene and Toluene Cations on Water Clusters

species	proton affinity[a]	species	proton affinity[b]	binding energy of OH to benzene[c]
phenyl	211	H_2O	167	16.5
benzyl	198	$(H_2O)_2$	195	
		$(H_2O)_3$	206	
		$(H_2O)_4$	215	
		$(H_2O)_5$	216	

[a] Reference 15. [b] Reference 16. [c] Reference 36.

The clusters of Bz with water were also investigated using the same techniques.[17−20] However, in contrast to the variety of chemical reactions that were reported using an environment of methanol molecules,[20] no chemical reaction could be detected for Bz$^+$−$(H_2O)_n$ clusters in the size domain studied ($n \leq 7$).[17−19] In particular, in contrast to the case of the toluene−water clusters, protonated water clusters were not observed. This point is in clear agreement with thermodynamical data (Table1) that predict the proton transfer reaction to be energetically forbidden for the small ($n < 4$) species, if one neglects the effects of solvation.

This difference in the behaviors of the Bz$^+$ and To$^+$ clusters suggests that the threshold for the reaction requires a water environment of larger size for Bz$^+$. The aim of the present work is to shed new light on the reactivity of [Bz−$(H_2O)_n$]$^+$ clusters, exploring the medium size range ($10 \leq n \leq 40$) and thus bridging the gap between the nonreactive small clusters and the reactions observed in the liquid phase.

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$Bz-(H_2O)_n$ clusters have been formed in a supersonic expansion, and the aromatic molecule has been photoionized within the cluster. The corresponding mass spectra have been recorded under various experimental conditions. The microsecond time scale evaporation dynamics has been observed and characterized by a kinetic energy analysis technique recently used in our group to study the aromatic−rare gas clusters.[21−23] These experiments have provided evidence for a mass spectrometric signature of the reactivity of Bz^+ in water clusters of medium (20−30) size range.

2. Experimental Method

The experimental setup, previously described in detail elsewhere,[21] combines a supersonic beam cluster source, a dye laser, and a reflectron-type time-of-flight mass spectrometer (TOF-MS).

Neutral mixed clusters are formed by a pulsed adiabatic expansion of a gas mixture containing room temperature vapor pressure of the aromatic molecule (Bz, To) and water. Helium is used as carrier gas at a backing pressure of about 2−3 bars. The vapor pressure of the aromatic molecule was low enough in order to prevent the formation of water solvated aromatic dimers and higher order polymers. The molecular beam is skimmed before entering the spectrometer chamber (pressure less than 10^{-6} Torr during operation) parallel to the MS axis. This collinear configuration allows us to detect efficiently a large mass range without changing the electrical parameters of the MS. In the first region of the mass spectrometer source (extraction region), the jet is crossed at a right angle by the UV output of an excimer-pumped dye laser (Lambda Physik, EMG 201 MSC and FL 3000) that is frequency doubled in a BBO crystal.

The solvated aromatic cations are formed by resonant two-photon ionization using a vibrational level (6^1 for Bz and 0^0 for To) of the S_1 state of the aromatic molecule as the intermediate state. The cluster absorption band is slightly blue-shifted relative to the monomer.[8,9,18,19] In the experiment, the dye laser is set at $\lambda = 258.52$ nm for benzene and $\lambda = 266.15$ nm for toluene. In contrast to small clusters, laser excitation does not cause mass selectivity because of the broad absorption bands of the clusters in the investigated size domain ($n > 10$). The cluster ions are then extracted and accelerated in the MS source and deflected from the jet axis in order to separate them from the neutral beam. After a field-free region (FFR) of 77 cm length, ions can be detected either in the linear mode on a rear mirror detector or in the reflectron mode after reflection in the electrostatic mirror and a flight in a second FFR. The corresponding mass spectra are recorded and averaged with a fast digital oscilloscope (LeCroy 9350).

The comparison between linear and reflectron modes provides us with information on the cluster ion population at two different times following the ionization.[21] The linear spectrum corresponds to the ionized cluster distribution at the exit of the spectrometer source (i.e. typically 1−3 μs after ionization in the present experiment and for the sizes studied), since this detection mode does not distinguish mother ions from fragments appearing in the first FFR. In contrast, the reflectron is designed to focus ions of the same mass onto the detector regardless of their kinetic energy Ec, as long as the Ec does not differ too much from the nominal value Ec° (typically $|Ec - Ec°| < 10\%$). For this reason, in contrast to the linear MS, the reflectron focuses at their true mass the daughter ions born in the first field-free region. The use of the reflectron thus yields the cluster population at the entrance of the electrostatic mirror, i.e., typically in the range of tens of microseconds after ionization.

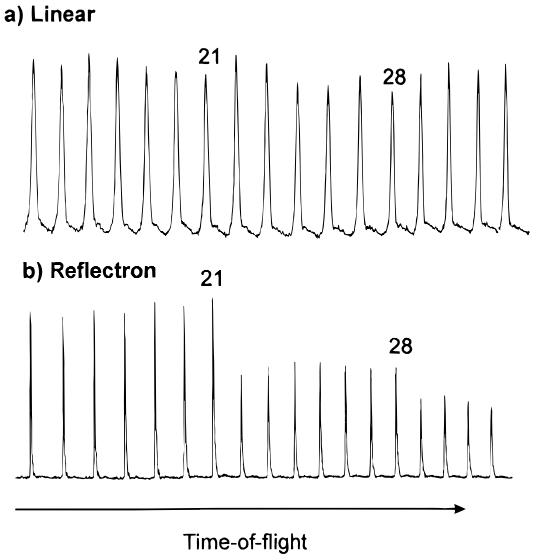


Figure 1. Mass spectra of laser-ionized $[Bz(H_2O)_n]^+$ clusters in the $n = 15-32$ range obtained for two detection modes: (a) linear, (b) reflectron. Time-of-flight of the $n = 21$ ion is 29.1 μs in (a) and 74.4 μs in (b). The two spectra have been rescaled for the sake of comparison.

The comparison between mass spectra recorded under linear and reflectron conditions allows us to have insight into the microsecond time-scale (metastable) evaporation processes occurring in the first FFR.

In order to study quantitatively the evaporation rates, we have also used a modified version[21] of a technique originally developed by Castleman and co-workers,[5] consisting of carrying out a kinetic energy analysis (KEA) of the ions with the help of the electrostatic mirror of the MS. Briefly, the modified technique consists of using the reflectron mirror as an electrostatic barrier which delays the ions according to their kinetic energy before detecting them on the rear mirror detector. Since daughter ions originating from the first FFR have the same velocity as their parents and consequently have a smaller kinetic energy, these ions will be more efficiently delayed when crossing over the electrostatic barrier and will be detected several hundreds of nanoseconds later. Using the KEA technique, we are able to measure the parent survival probability (or metastable decay rates) of the cluster ions during their flight in the first FFR, i.e. during a typical 2−40 μs time window.

3. Experimental Results

3.1. Mass Spectra of Benzene−Water Clusters in the Size Domain $n = 10-40$.

Mass spectra of the laser-ionized $Bz-(H_2O)_n$ clusters have been obtained in both linear and reflectron detection modes (Figure 1a,b).

3.1.1. Linear TOF Spectrum. The mass spectrum of the $[Bz-(H_2O)_n]^+$ clusters obtained in the linear detection mode (Figure 1a) is composed of a unique series of mass peaks, characterized by a rather regular intensity variation. The resolution remains modest ($\Delta m/m \sim 150$ at $n = 20$), so that the unambiguous assignment of the mass, within the precision of 1 amu, is difficult. Nevertheless, it clearly does not fit a series of pure protonated water clusters, like observed following the ionization of small $To-(H_2O)_n$ clusters.[7−9] This first result already shows no apparent signature of a similar reaction for benzene.

3.1.2. Reflectron TOF Spectrum. The mass spectrum of the $[Bz-(H_2O)_n]^+$ clusters obtained in the reflectron detection mode is given in Figure 1b. It is composed of a unique series of mass peaks and shows a better resolution than the linear mode

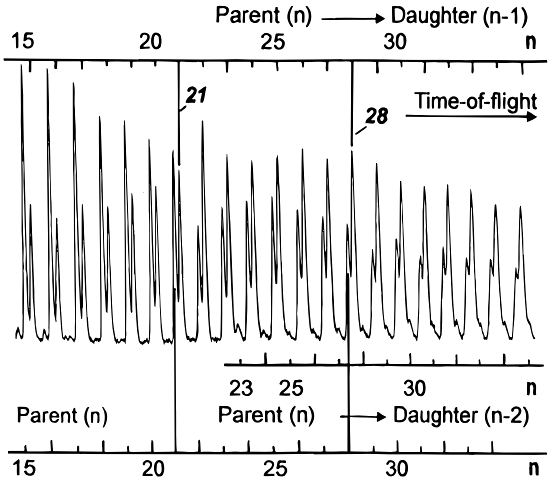


Figure 2. Mass spectrum of laser-ionized $[Bz(H_2O)_n]^+$ clusters using KEA; the early component of the doublet series corresponds to those ions which did not evaporate in the field-free region of the mass spectrometer (typical time window 2−40 μs); the late component is composed of clusters having lost a water molecule during the same time window. The minor series corresponds to the loss of two water molecules. In the experiment, the ion nominal kinetic energy is 1792 V and the barrier energy is set to 1582 V. Time-of-flight of the $n = 21$ ion is 30.6 μs.

($\Delta m/m \sim 2000$ at $n = 20$). A precise assignment of the peaks is possible if one accounts for small effects like the initial kinetic energy of the clusters, induced by the collinearity of the molecular jet with the spectrometer axis. This analysis allows us to assign the band series to species having exactly the mass of $Bz-(H_2O)_n$ clusters. The most striking difference between the two spectra of Figure 1 is in the intensity distributions. In contrast to the linear mode, the spectrum recorded in reflectron mode exhibits very prominent anomalies at $n = 21$ and 28, characterized by severe intensity drops between 21 and 22 as well as between 28 and 29. Such significant intensity drops are reminiscent of the so-called magic numbers encountered in the mass spectra of numerous atomic[24] or molecular clusters.[21−23,25−28] Since, as emphasized above, the two distributions actually monitor two different time delays after ionization, one should conclude that the process responsible for these intensity anomalies is unimolecular decay, i.e., evaporation of water molecules from the cluster ions.

3.2. Characterization of the Evaporation in the Ionized Benzene−Water Clusters. In order to characterize the evaporation process in the field-free region, we have performed KEA experiments. The KEA spectrum of the $[Bz-(H_2O)_n]^+$ clusters (Figure 2) exhibits two main series of mass peaks of similar intensities and slightly shifted one relative to the other. The first one is assigned to parent ions which did not evaporate in the first FFR. The second one is composed of daughter ions, i.e., ions having lost some molecules in the FFR. The time delay between the parent and daughter ions (~200 ns) allows us to assign the second series to ions that have evaporated one water molecule. The similar intensities of these two series suggests that the evaporation probability is not negligible. In addition, a third minor series, corresponding to the loss of two water molecules, appears with significant peak intensities in the mass range above $n = 23$.

The measurement of the parent and fragment intensities (I_p and I_f, respectively) for each mass allows us to derive the parent ion survival probability $I_p/(I_p + I_f)$ in the FFR (Figure 3). The two severe drops at $n = 22$ and $n = 29$ indicate a strongly size-dependent evaporation process. In particular, these results show that the $n = 22$ and 29 species lose one water molecule with high probability. This is also in accordance with

(1) the size threshold for the loss of two water molecules at $n = 23$. The $n = 23$ and 30 cluster ions indeed evaporate one water molecule with an appreciable probability, leading to $n = 22$ and 29 daughter species that have themselves a large probability to evaporate another water molecule.

(2) the large abundances observed in the mass spectrum at $n = 21$ and $n = 28$, since for these sizes the contributions arising from $n + 1$ and $n + 2$ clusters widely overcome their own evaporation toward the n - 1 size channel.

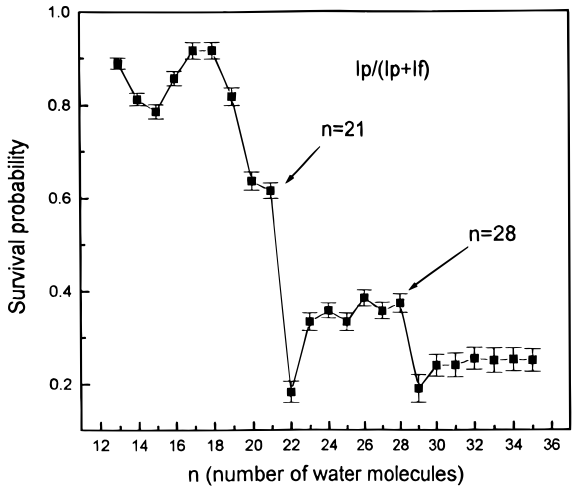


Figure 3. Size dependence of the $[Bz(H_2O)_n]^+$ survival probability obtained from a typical KEA spectrum.

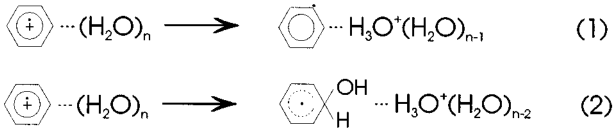
These results clearly show that the magic numbers arise from a very size-specific evaporation process, occurring after ionization. The internal energy thereby dissipated can be assigned to a cluster rearrangement following ionization due to the expected large geometry change between neutral and ion species,[29,30] perhaps accompanied by a reactive exothermic process. It should be noted that a careful study of the ion signal as a function of the laser intensity has shown that the $[Bz-(H_2O)_n]^+$ ions and Bz^+ exhibit the same dependence, showing that the cluster ions are produced by a two-photon process. In particular, the absorption of a third photon by the cluster ions can be excluded.

3.3. Assignment of the Magic Numbers. The observation of magic numbers in the mass spectra of clusters is often related to the existence of "magic structures", in the sense that for these structures the evaporation energy is larger than for clusters of larger size. As an example, the appearance anomalies observed at $n_M = 13, 55, 149, ...$ in the mass spectra of rare gas clusters have been assigned to successive closures of the geometric shells around an icosahedral core,[24] which causes a large discontinuity in the evaporation energies. Magic structures have also be invoked to explain the mass spectra of molecular clusters.[21−23] For instance, the mass spectrum of mixed clusters (M^+S_n, where M is an aromatic molecule like benzene, aniline, ... and S is a nonpolar solvent molecule (N_2, CH_4, CO, or a rare gas atom) have been shown to exhibit a unique magic number, which has been assigned to a saturation of the first solvent shell around the molecular cation.[22]

Also in the $Bz-(H_2O)_n$ case we suggest to assign the observed magic numbers to well-defined cluster structures.

Two such structures could *a priori* account for the magic numbers in the benzene−water clusters: (i) a saturated shell of water molecules around the benzene cation and (ii) a magic water microdroplet with the benzene moiety lying on its surface. The first possibility can actually be ruled out for the following reasons. A shell closure would lead to a unique prominent magic size,[21−23,31] which is in clear disagreement with the present observation; moreover, the most probable magic number in this size range would not be 21 but 20, corresponding to the clathrate structure already invoked in the case of metallic ion−water clusters.[31] In addition, the same experiments carried out on the toluene−water systems (Figure 4) show that these clusters exactly behave in the same way as $[Bz-(H_2O)_n]^+$ clusters. In particular, magic numbers appear only in the reflectron spectrum and at the same *n* as for Bz. According to the different volumes of Bz^+ and To^+,[22] the magic numbers observed probably do not correspond to the closure of a solvation shell of water molecules around the aromatic cations.

Finally the strongest argument for the assignment of the magic numbers to a droplet-like structure of the water moiety with the aromatic sitting on the surface arises from the comparison of the mass spectra of the aromatic cation−water clusters (Figure 4) with those of protonated water clusters.[25−28] Spectra of protonated water clusters also exhibit magic numbers having the same characteristics: appearence at a microsecond time scale and for the same size as the species studied in the present work, $n = 21$ and 28. The $n = 21$ and 28 magic numbers have been assigned to the existence of compact $H^+(H_2O)_n$ forms, in which a protonated core (H_3O^+ or $H_2O\cdots H_3O^+$, respectively) is encaged in a close shell (clathrate) organized according to a dense hydrogen bond network.[25−28] This striking similarity suggests that in ionic benzene− or toluene−water clusters a chemical reaction has occurred between the aromatic cation and the water cluster leaving the water molecules organized in a same way as in a *protonated* water cluster. Since the mass measurements indicate that the aromatic cation−water cluster ions correspond to the mass series of $Bz-(H_2O)_n$ clusters, one has to conclude that a proton transfer reaction takes place within the cluster without any mass loss, except eventually evaporation of water molecules. Consequently the mass conservation implies that the aromatic reaction product should be either the corresponding neutral radical (phenyl or benzyl) or the adduct formed between the neutral aromatic and an OH radical. In the former case, the radical should be bound at the surface of the protonated water cluster (reaction 1); in the latter case, the adduct should be in the surface, in the sense that the OH and H moieties of the adduct take part to the first solvation shell of the protonated water ion (reaction 2).



4. Discussion

The present experiment gives evidence that aromatic cations can react in medium-sized clusters (typical size range $n = 10-40$), without dramatic effects upon the mass spectra, i.e., without apparent mass change except evaporation of solvent molecules. Indeed in the present cluster experiment magic numbers are the only mass spectrometric fingerprint of the chemical reaction in the aromatic cation−$(H_2O)_n$ clusters. Therefore monitoring magic numbers turns out to be an elegant way to probe a rather discrete chemical reaction with a mass spectrometer (in the present case, an intracluster proton transfer), even if this observation does not allow us to distinguish between the two possible final products.

4.1. A Microscopic Model of the Cluster Experiment. The sketch of the experiment at the microscopic scale can be presented as follows:

(1) Neutral clusters are formed in the molecular jet. They are composed of a rather compact water cluster, with the aromatic molecule on its surface. The binding is formed essentially by the interaction between the aromatic π−electrons and the outer water molecules of the cluster, which have their hydrogen atoms oriented toward the aromatic ring.[29]

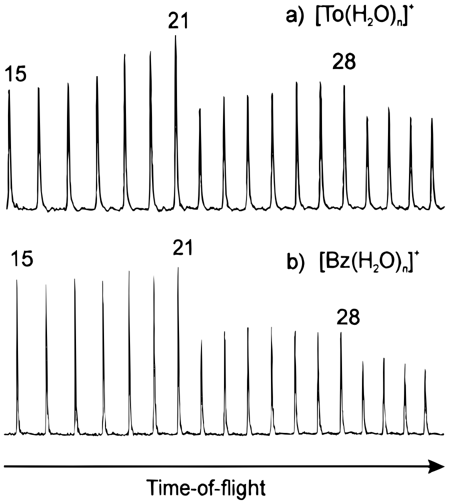


Figure 4. Reflectron mass spectra of laser-ionized $[To(H_2O)_n]^+$ (a) and $Bz(H_2O)_n{}^+$ (b) clusters. The two spectra have been rescaled for sake of comparison.

(2) The aromatic molecule is ionized by the laser light. However, the neutral cluster geometry does not correspond to that of the minimum energy ionic cluster, because of the large charge−dipole interaction, which characterizes the ionic state.[17] The water molecules thus rearrange in the field induced by the cation, by flipping over in order to minimize their charge−dipole interaction. During this rearrangement potential energy is converted into kinetic energy, which leads to a significant heating of the cluster. Recent unpublished molecular dynamics simulations by Gaigeot et al. on the ionization of $Bz-(H_2O)_{10}$ suggest temperature increases as high as ∼150 K.[32]

(3) Before the encaging of the aromatic cation by the water molecules occurs (which likely corresponds to the minimum energy conformation of the ionic cluster[32]), the chemical reaction takes place and leads to the formation of a protonated water cluster, with the final aromatic product attached on its surface.

(4) The large amount of internal energy, due to both the ionization and the exothermicity of the reaction, is dissipated by successive evaporations of water molecules. As emphasized by Klots, the evaporation rates decrease dramatically with time.[33,34] Numerous evaporations can take place in the first nanosecond following ionization. A rough evaluation from excess energy and water−water interaction energy suggests a number of ∼7−10 evaporations.

(5) Only very late evaporation processes are observed in the microsecond time window of the mass spectrometer. The distribution in linear mode ($t < \sim 2\ \mu s$) is still smooth because clusters are hot enough to be liquid and thus do not have a well-defined structure. However after several tens of microseconds, the evaporation events have cooled the cluster efficiently enough for the appearance of a solid-like "magic" structure, resulting in magic numbers. This can be considered in many respects as the cluster equivalent of a bulk solidification process.

In this scenario, the cluster clearly is a confining structure capable to bring together the reactants and to isolate reaction products; moreover, it behaves like a small thermodynamic heat bath, by absorbing the energy excess and regulating the temperature by successive evaporations.

4.2. Reaction Mechanism. The present results do not allow us to distinguish between the two possible aromatic products

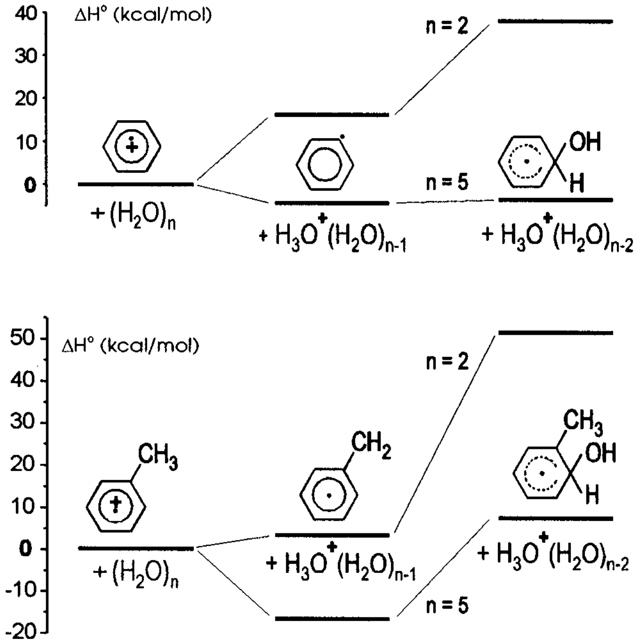


Figure 5. Energetics of the reaction channels of the $Bz^+ + (H_2O)_n$ and the $To^+ + (H_2O)_n$ systems expressed relative to the entrance channel for two cluster sizes: $n = 2$ and 5. The lines connect species belonging to the same size, without any special meaning about reaction mechanisms. The thermodynamic data required have been taken from Table 1, completed by proton solvation data extracted from ref 35. In these data the unknown solvation energy of the aromatic moiety has not been taken into account.

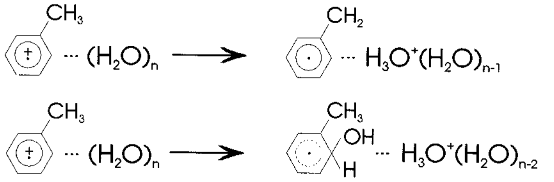
of the reaction, namely, the radical (channel 1) or the OH adduct (channel 2), and hence cannot bring very precise information about the reaction mechanism. However reaction energetics (Figure 5, Table 1) gives us some clues for discussion, even if these data do not account for the solvation effects of the benzene ring by the water cluster.

In the case of benzene cations, Figure 5 indicates that the two reactions channels are forbidden for the small clusters. However, as soon as $n = 5$, both channels are energetically allowed, and their energetics appears to be very similar. Nevertheless some arguments suggest that the reaction 2 actually takes place.

The fact that, in the present evaporation measurements, we do not observe any evaporation of the aromatic moiety from the cluster suggests that the binding energy of the product to the water cluster exceeds that of a water molecule. This can be easily understood if the final product is an OH adduct, since its OH and H adduct moieties can participate in the network of hydrogen bonds within the water cluster.

Experiments in solution have only reported the formation of the OH adduct in the case of benzene.[11,13] This suggests that in solution reaction 2 channel 2 is favored. It could be the same for medium size range clusters. This conclusion is in qualitative agreement with the effect of solvation for the small clusters: Figure 5 shows clearly that reaction 2 is much more sensitive to solvation than reaction 1.

In the case of toluene cations, the variation of the proton affinity of water clusters with the cluster size (Table 1; Figure 5) suggests that the proton transfer mechanism from the methyl group (reaction 1′), proved for the small clusters,[8,9] should be also valid for larger clusters. In this case the final product of a direct proton transfer would be the stable benzyl radical. However, the occurrence of the second mechanism (2′), which leads to the formation of a neutral toluene–OH adduct, already reported from the experiments carried out in neutral aqueous solutions,[12] should be considered. Figure 5 suggests that if this mechanism can be rejected for small clusters, it can become thermodynamically allowed for larger clusters, in agreement with the observation that solvation effect seems to be larger for channel 2 than for channel 1. Moreover mechanism 2′ is again supported for the medium size range clusters by the same arguments as for benzene, i.e., the fact that the evaporation of the benzyl radical from the cluster is never observed.



(1′)

(2′)

Additional experiments are in progress in our laboratory in order to better characterize the mechanisms involved. Ongoing experiments will involve a two-color ionization scheme which will be interesting to investigate eventual temperature effects by a better control of the excess energy deposited in the ion by the ionization process. Moreover, pump–probe experiments will allow us to elucidate the nature of the final product.

5. Conclusion

The present result indicates that ion–molecule reactions can happen in large ($n < 30$) clusters without spectacular manifestations in the mass spectra. The mass spectrometric diagnosis using a reflectron-type mass spectrometer combined with kinetic energy analysis is demonstrated to provide a new method to monitor intracluster reactions, leading to the formation of a protonated water subcluster in the $n = 22-28$ size range.

The comparison of the present results on medium-sized clusters with those on the small species[7–9,17–19] illustrates the existence of two size effects in the chemical reactivity of aromatic cations bound to a water environment:

(1) In the case of the Bz cation, a reaction is found to occur for $n = 20-30$, whereas small $Bz^+(H_2O)_n$ ($n < 8$) clusters are known not to react.[17–19]

(2) In the case of toluene, for which reaction is known to take place as soon as $n = 3$,[7–9] the separation of the reaction products is not observed for large clusters. This might either illustrate the role of a thermostat played by the large water clusters, which are able to dissipate the excess energy, or indicate that the reaction mechanism changes when passing from small ($n \sim 3-6$) to large ($n \sim 25$) clusters.

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