Protonated Benzene Structure

Infrared Fingerprint of Protonated Benzene in the Gas Phase**

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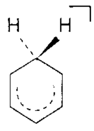
$C_6H_7^+$ ions are obtained from the gas-phase protonation of benzene, namely, by the prototypical aromatic electrophilic addition reaction. The formation of protonated benzene has therefore attracted several investigations aimed at ascertaining the thermodynamic and reactivity features of the product ion besides its structure.[1] It is now widely recognized that the stable structure of protonated benzene is a σ complex species (**1**), whereas the edge-protonated structure **2** is a first-order saddle point 25–38 kJ mol^{-1} higher in energy and the face-centred π complex (**3**) is a second-order saddle point still higher in energy, at 200 kJ mol^{-1}.[2]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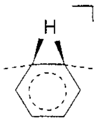
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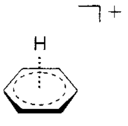
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The experimental proton affinity[3] of benzene (750 kJ mol^{-1}) is nicely matched by the theoretical value of 744–761 kJ mol^{-1},[2] thus proving that **1** is the stable protonated benzene ion. The edge π complex **2** is a transition structure for a 1,2-H shift within **1**, a process which leads to the scrambling of the seven H atoms. This process was first observed by dynamic NMR spectroscopy in superacid media.[4] The kinetic features of the process reported for gaseous benzenium and related arenium ions[5] are consistent with activation energies close to the computed value of 25–38 kJ mol^{-1}. Also, a species resembling **2** appears as the lowest energy structure calculated for the benzene–oxonium complex.[6] Finally, the face-centred π complex **3** has been invoked to account for the collision-induced decomposition behavior of protonated benzene ions by loss of H atoms.[7]

In this context the possibility of a direct spectroscopic characterization of $C_6H_7^+$ ions appeared to be a desirable contribution to settling the argument over the structure of the gaseous benzenium ion. Spectroscopic investigations of gaseous ions face the problem of their typically low concentration. Recently, the infrared spectrum of the $C_6H_7^+$ ion was recorded by Solcà and Dopfer by using tunable IR laser pulses generated by an optical parametric oscillator laser system.[8] Another interesting alternative to overcome the inherent problem of the low concentration of ions is to study the wavelength dependence of IR multiphoton dissociation (IRMPD).[9] Infrared free electron laser (FEL) light sources[10] have been shown to be suitable to activate IRMPD.[11] In the present work, the Centre Laser Infrarouge Orsay (CLIO) FEL facility has been used. It is based on a 10 to 50-MeV electron accelerator that yields IR radiation fulfilling the requirements of both a high peak power and a relatively small bandwidth (up to 0.3 %). The most interesting characteristic is its large tunability (3–90 μm) which provides, in particular, access to the fingerprint region ($\tilde{\nu} = 600$–$1500\ \text{cm}^{-1}$). The present work thus provides an interesting complement to the work of Solcà and Dopfer on $C_6H_7^+$ ions which yielded information on the CH stretching region ($\tilde{\nu} = 2700$–$3200\ \text{cm}^{-1}$).[8]

The FEL IRMPD has been applied to $C_6H_7^+$ ions produced and stored in an ion cyclotron resonance (ICR) ion trap. FT-ICR is in fact a technique of choice for complex ion manipulation and storage which takes advantage of a high mass resolution.[12] The experimental setup, which has been described elsewhere,[13] uses a mobile ICR analyzer[14] based on a permanent magnet of 1.25 Tesla. The laser light is focussed at the center of the ICR ion trap using a spherical mirror of 1 m focal length; the laser spot diameter has been estimated to be about 400 μm.

Quantum chemical calculations are needed to characterize the possible isomers of the ion of interest and determine the corresponding IR absorption spectrum, which can then be compared with the experimental IR spectrum derived from the wavelength dependence of the IRMPD process so that the identity of the structure of the ion trapped in the ICR cell could be determined. The expected vibrational spectrum has been calculated using the B3LYP6-311++G** method.[15] The three significant species (**1**–**3**) on the potential energy surface of the $C_6H_7^+$ ion have been characterized, and good quantitative agreement found with recent reports.[2] In particular, the σ complex **1** has been found to be the energy minimum, the bridged structure **2** being a transition state lying 42 kJ mol^{-1} above the σ complex **1**, while the π complex **3** has been found to be a second-order saddle point.

As shown in Figure 1, the photodissociation process appears to involve $C_6H_7^+$ ions, which undergo loss of H_2 with a yield of 10 to 25 %, while the intensity of the $C_6H_6^{+\bullet}$ ions, also present in the ICR cell, stays approximately constant as a function of the infrared energy. Loss of H_2 is the lowest energy dissociation channel for the $C_6H_7^+$ ions. The process is known to involve negligible activation energy,[16] which is in agreement with quantum chemical calculations.[2c] The barrierless dissociation to $H_2 + C_6H_5^+$ is reported to require 296 kJ mol^{-1}.[2c] This value means that the absorption

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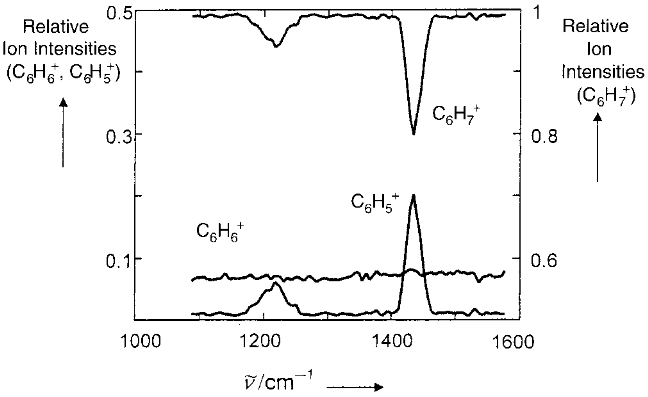

Figure 1. Relative ion intensity following IRMPD as a function of the radiation wavenumber. The left scale refers to ions with *m/z* 77 and 78, the right scale to the ion with *m/z* 79.

of at least ten photons is needed to provide sufficient internal energy for $C_6H_7^+$ ions to undergo dissociation into H_2 + $C_6H_5^+$ ions

The relative intensity of the $C_6H_5^+$ product ions, which is proportional to the normalized fragmentation yield, is shown in Figure 2 as a function of the radiation wavelength, thus providing an IR spectrum of the absorbing ion. The experimental pattern is viewed together with the calculated IR spectrum of **1**. Whereas significant red shifts have been previously observed,[11b] relative to the expected fundamental absorption transitions in the harmonic approximations, the two bands observed experimentally at $\tilde{\nu} = 1228$ and 1433 cm^{-1} nicely match with the two most intense absorptions determined theoretically at $\tilde{\nu} = 1237$ and 1434 cm^{-1} for the σ complex. The band at $\tilde{\nu} = 1237$ cm^{-1} corresponds to CH_2 scissoring, while the band at $\tilde{\nu} = 1434$ cm^{-1} corresponds to the in-plane CH bending of the hydrogen atoms in the position *meta* to the methylene group. It may be noted that the expected absorption at $\tilde{\nu} = 1582$ cm^{-1}, which corresponds to a ring deformation of the $C_6H_7^+$ ion and is calculated to be less intense than the transitions at $\tilde{\nu} = 1237$ and 1434 cm^{-1}, is not observed. This absence could be related to the nonlinear nature of the IRMPD at low laser fluence which had previously been observed with the present experimental setup.[13]

The IRMPD of a multiply deuterium-labeled benzenium ion was investigated to test the results obtained with this approach and check the reliability of the methodology adopted. The $C_6D_6H^+$ ions were formed by protonation of C_6D_6 and found to undergo wavelength-dependent loss of HD/D_2 as shown in Figure 3. Once again the dominant IR absorption bands predicted for the σ complex are active in inducing IRMPD at $\tilde{\nu} = 1439$ and 1572 cm^{-1} (theoretical values: $\tilde{\nu} = 1410$ and 1534 cm^{-1}, respectively). As can be seen in Figure 3, the predicted transition at $\tilde{\nu} = 2081$ cm^{-1}, which corresponds to the symmetric CH stretch of the methylene group, is not observed experimentally. As in the case of the $C_6H_7^+$ ion, this transition is expected to be less intense than the two observed transitions, and this could be the origin of a less efficient IRMPD in the corresponding region. It is interesting to compare the branching of HD/D_2 loss in the present IRMPD experiments with the collision-induced dissociation (CID) of $C_6D_6H^+$ ions formed by mild protonation with oxonium ions (and H/D exchange processes) in H_2O/C_6D_6 (or D_2O/C_6H_6) mixtures in flowing afterglow–selected ion flow tube (FA-SIFT) experiments (Table 1).[17]

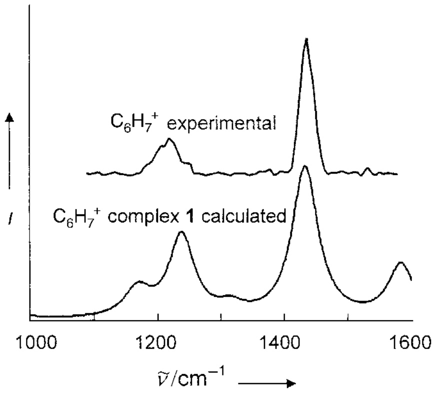

Figure 2. IRMPD spectrum of the $C_6H_7^+$ ion.

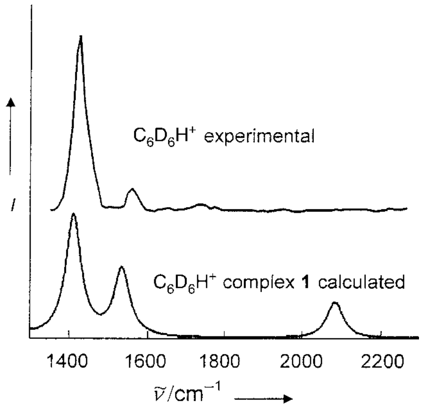

Figure 3. IRMPD spectrum of the $C_6D_6H^+$ ion.

Table 1: Dissociation of $C_6D_6H^+$ ions.

Ion precursors	Method	HD loss	D_2 loss	Ref.
statistical		29	71	[17]
CH_4/C_6D_6	IRMPD at 1439 cm^{-1}	38	62	this work
CH_4/C_6D_6	IRMPD at 1572 cm^{-1}	39	61	this work
H_2O/C_6D_6[a]	CID	31	69	[17]
H_2O/C_6D_6[b]	CID	30	70	[17]
D_2O/C_6H_6[a]	CID	35	65	[17]

[a] CID performed in FA-SIFT experiments. [b] CID performed in FA-SIFT triple quadrupole experiments.

Interestingly, the relative amount of HD/D_2 loss is the same (38-39/62-61) for the two photon energies ($\tilde{\nu} = 1439\ \text{cm}^{-1}$ and $1572\ \text{cm}^{-1}$), allowing for IRMPD. These values are close to the ones statistically expected for the complete scrambling of hydrogen atoms within benzenium ions.[18] In particular, the single collision conditions prevailing in the CID performed in the FA-SIFT-triple quadrupole should ensure that the dissociating ions retain their original structure, because any possible isomerization is unlikely in the time frame of the process. It may thus be concluded that protonated benzene ions, irrespective of their formation—either by proton transfer followed by a few seconds delay in the ICR cell or by milder protonation in a high pressure (ca. 0.3 Torr) FA source—show similar reactivity features. They undergo fast equilibration of the seven hydrogen atoms and show a similar branching of HD/D_2 loss when the $C_6D_6H^+$ ion is the sampled species. These ions are unambiguously characterized as σ complexes.

In conclusion, the present IRMPD results confirm the σ complex structure of protonated benzene, $C_6H_7^+$, which is in contrast with recent IRMPD evidence showing the preference for a π structure for benzene–metal-cation complexes.[11b,19] Furthermore, the reported study proves the potential of the experimental setup (in which a FT-ICR is coupled with an infrared FEL) combined with the theoretical calculation of the IR spectra of the species being considered.[11c,13] In the near future, the interface of appropriate ion sources will extend the capabilities towards probing the structure of ionic complexes of biomolecules.

Experimental Section

The experiments were performed by letting the required reagent gases into the ICR cell through pulsed valves. The ionization of methane, admitted into the cell at 1.4×10^{-6} Torr for 100 ms, and ensuing ion–molecule reactions yielded CH_5^+ and $C_2H_5^+$ ions. These strong Brønsted acids[3b] were used to protonate benzene, which was subsequently introduced at 4.2×10^{-7} Torr for 100 ms. A reaction time of about 4 s was allowed for the proton transfer reaction to occur and the ensuing ion population, comprised of $C_6H_7^+$ ions and about a 10 % fraction of $C_6H_6^+$ ions, was then irradiated for about 5 s. IRMPD resulted from firing trains of "macropulses" at a repetition rate of 25 Hz. Each train was 8-μs long and contained 500 "micropulses" a few picoseconds long each. Under these conditions the typical peak power (and energy) delivered during the micropulse and macropulse are 20 MW (50 μJ) and 3 kW (25 mJ), respectively.

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