The Face-centred π Complex Isomer of the Benzenium Ion is Probably the Most Stable Form in the Gas Phase: Experimental Evidence

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Two stable isomers of the benzenium ion are identified by CID MS, the most stable of which appears to be the face-centred π complex.

Arenium ions are important intermediates in electrophilic substitution reactions and have long been of great interest.[1] The benzenium ion, $C_6H_7^+$, is the simplest of this class. Although difficult to make in solution Olah *et al.*[1,2] showed this species to be the σ complex **II** using NMR spectroscopy. The benzonium form **III** is inferred to be present as the transition state for intramolecular proton transfer around the ring at *ca.* 40 kJ mol^{-1} above the ground state. The ion is easily made and observed in the gas phase.[3] The physical chemical measurements on it, made so far, are also consistent with its structure being the σ complex.[4–6]

The π complex **I**, in which the proton is coordinated with the entire π system, has been speculated upon[1,2,7,8] but never seen. On the other hand the existence of similar π complexes involving other electrophiles is well established.[9]

The many theoretical (*ab initio*) molecular orbital (MO) calculations, carried out so far,[7,10,11] also point to the σ complex as the most stable form, the theoretical energy of **I** being very much higher in energy (350–400 kJ mol^{-1}) than the other forms and not stable with respect to the edge-protonated species.[11]
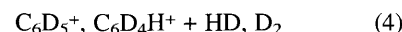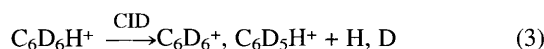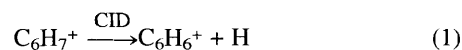
It is very surprising therefore that we have obtained experimental evidence, not only of two stable isomers of the benzenium ion in the gas phase, but that the most stable form is probably the face-centred π complex **I**.

The experiments were carried out in an ion–molecule reactor apparatus[12] consisting of a temperature and pressure controlled chemical-ionisation source attached to a forward geometry double focusing mass spectrometer modified to allow collision-induced decomposition (CID) MS using the *B/E* Linked Scanning technique.[13,14] The benzenium ions were made by chemical ionisation of benzene (or [$^2H_6$]benzene) mixed into methane gas.[3]

The species $C_6H_7^+$ (or $C_6D_6H^+$) was the dominant ion in the chemical ionisation mass spectrum under all conditions studied here and the $C_6H_7^+$:$C_6H_6^+$ peak ratios were in the region of 15:1. Contributions to the $C_6H_7^+$ peak from the isobaric $^{13}C^{12}C_5H_6^+$ ion were therefore <0.5%. Under high resolution mass spectrometer conditions no other isobaric ion could be detected.

CID mass spectra of $C_6H_7^+$ (at m/z = 79) and $C_6D_6H^+$ (m/z = 85) are shown in Fig. 1. The major fragmentations induced

by collision at 6 keV with N_2 are the loss of H and H_2 from $C_6H_7^+$ [eqns. (1) and (2)] or H, D, HD and D_2 from $C_6D_6H^+$ [eqns. (3) and (4)], these being the least endoergic processes.

$$C_6H_7^+ \xrightarrow{CID} C_6H_6^+ + H \tag{1}$$

$$C_6H_5^+ + H_2 \tag{2}$$

$$C_6D_6H^+ \xrightarrow{CID} C_6D_6^+, C_6D_5H^+ + H, D \tag{3}$$

$$C_6D_5^+, C_6D_4H^+ + HD, D_2 \tag{4}$$

The energy thresholds for H and H_2 loss are [15] 339 and 287 kJ mol^{-1}. In competition from the same isomer the greatest degree of fragmentation usually occurs for the lowest energy process unless there is a significant rearrangement required. Loss of H_2 from **II** is therefore expected to be dominant over loss of H, as occurs, for example, during the CID of ring-protonated fluorobenzene.[14]

It is obvious from Fig. 1 that the efficiency of H to H_2 loss varies dramatically with the temperature of the reaction mixture. At low temperatures H loss occurs much more readily than loss of H_2, but decreases to the level expected on the basis of their respective endoergicities as the temperature is increased. The $C_6D_6H^+$ spectra closely reproduce the behaviour of $C_6H_7^+$. The data for H:H_2 and H:D *versus* temperature for the two systems are shown in Fig. 2. The high H-loss peak in the spectrum of $C_6D_6H^+$ shows that at low temperatures the added proton has become attached to a site on the molecule which is quite distinct from the edge-bound D atoms. (Kinetic isotope effects are unlikely to be an issue here, because although it may cause a higher H:D ratio during CID, the high energy CID efficiency is most unlikely to be changed by temperature;[16] in any case the effect is not much different to that measured in protonated benzene). As the temperature increases the H:D ratio decreases to a value of 1:3, much closer to that expected (1:6) if complete scrambling had occurred.

This behaviour can be rationalised if the ion beams contain a mixture of two distinguishable isomers of protonated benzene
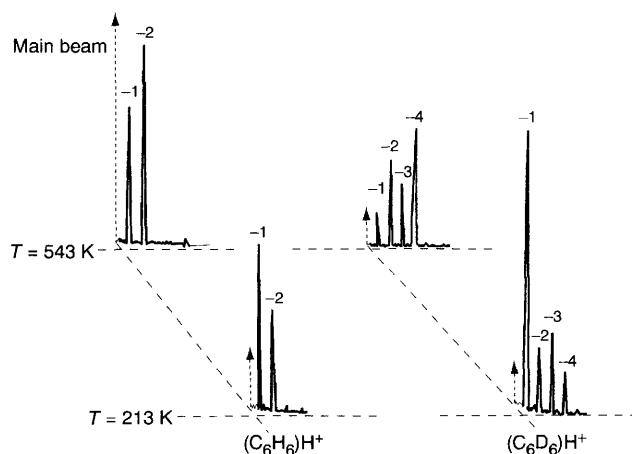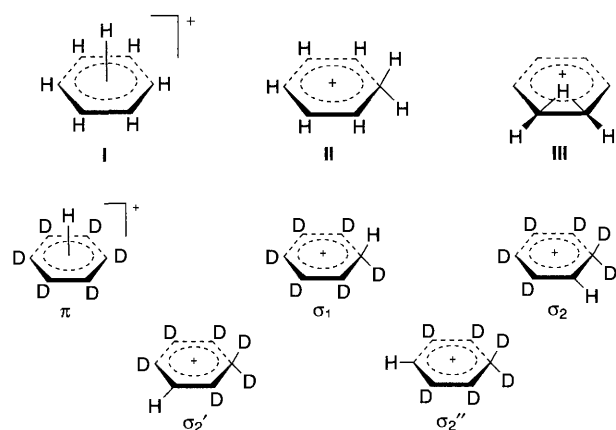

Fig. 1 Collision-induced decomposition spectra of $C_6H_7^+$ and $C_6D_6H^+$ created at different temperatures in methane gas (containing *ca.* 1000 ppm benzene or [$^2H_6$]benzene) in the chemical ionisation source at a pressure of 2 Torr

(or [^{2}H$_6$]benzene). At low source temperatures the dominant isomer has a structure in which the added proton is effectively isolated from the edge-bound hydrogens. It is difficult to envisage any structure other than the face-centred π complex **I**, which could account for this.

For C$_6$H$_7^+$ it is assumed therefore that H comes mainly from π, but with a small contribution from σ, whilst H$_2$ loss is only produced from σ. For C$_6$D$_6$H$^+$ it is assumed that H comes mainly from π, but with a small contribution from σ, but that D comes only from σ (there are four different σ complex isomers of C$_6$D$_6$H$^+$—σ$_1$, σ$_2$, σ$_2'$ and σ$_2''$—but only σ, will contribute significantly to loss of either D or H). If, as seems likely,[14] the different benzenium ions are in equilibrium with each other, then the model is simply represented by eqn. (5):
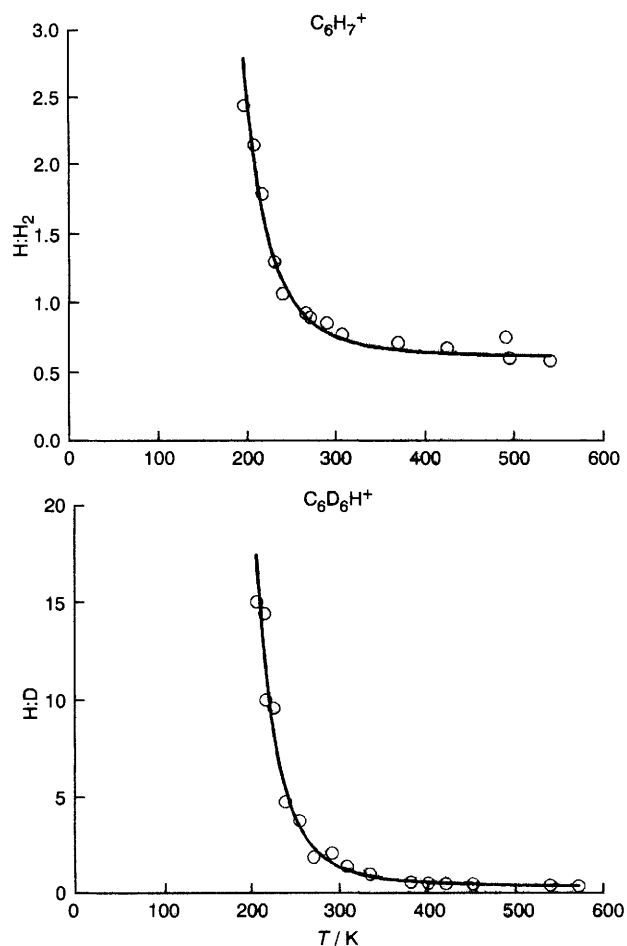
$$\pi \Leftrightarrow \sigma \tag{5}$$

Fig. 2 Plot of the ratio H : H$_2$ and H : D *versus* temperature obtained in the C$_6$H$_7^+$ and C$_6$D$_6$H$^+$ systems respectively at a pressure of 2 Torr in methane; also showing the fit of the theoretical models

Then, eqns. (6) and (7) hold,

$$\frac{H}{H_2} = \frac{\alpha[\pi] + \beta[\sigma]}{\gamma[\sigma]} = a + b \exp(x/T) \tag{6}$$

$$\frac{H}{D} = \frac{\theta[\pi] + \phi[\sigma]}{\xi[\sigma]} c + d \exp(x/T) \tag{7}$$

where α, β, γ, θ, φ and ξ are all relative cross-sections for the respective collision-induced fragmentations, and *a*, *b*, *c* and *d* are therefore constants; *T* is the temperature in K. The best fits for the C$_6$H$_7^+$ and C$_6$D$_6$H$^+$ data are obtained when *x* = 1600 and 1960 K respectively, *i.e.* when the apparent energy differences between the π and σ complexes are 13.3 and 16.3 kJ mol^{-1} respectively.

The main area of doubt is in the effective kinetic temperature of the ions, likely to be higher than the neutral gas because they are reacting in a plasma. Experiments are being devised to test the degree of uncertainty introduced by this and to allow suitable calibration. Therefore the present value of *ca.* 16 kJ mol^{-1} is offered as a tentative estimate only of the difference in energy between the two stable benzenium ion isomers. This finding may have important ramifications in the understanding of the very rapid intramolecular reactions observed in multiple aromatic ring systems.[17]

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