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Gas-Phase Spectroscopy of Protonated Hexamethylbenzene and Hexamethyl(Dewar benzene)

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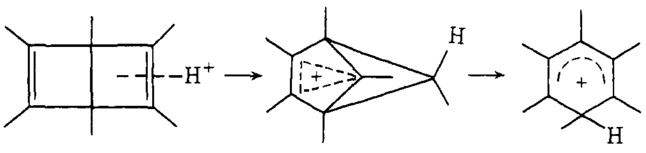
Abstract: Techniques of photodissociation spectroscopy indicate that the gas-phase protonated hexamethyl(Dewar benzene) cation rearranges within less than a few seconds to the protonated hexamethylbenzene structure. The spectrum of protonated hexamethylbenzene is analogous to those of other gas-phase protonated methylbenzenes, and is similar in peak position (with a small blue shift) and intensity to the solution spectrum of hexamethylbenzenium ion. The proton affinities of the ^1L_b and ^1L_a excited states of hexamethylbenzene are apparently higher by 30 and 28 kcal, respectively, than that of the ground state.

Hogeveen and Volger[1] found that in solution protonated hexamethyl(Dewar benzene) ion I rearranges to the bicyclic structure II at low temperature, and that II rearranges irreversibly to protonated hexamethylbenzene III at temperatures near room temperature with an Arrhenius activation energy of 24.3 kcal. The various rearrangements and possible cation structures issuing from initial formation of I have been the subject of extensive investigation and discussion.[2] It is clear that III represents the most thermally stable of structures I-III, but the potential surface has a local minimum for II which can allow its observation under appropriate conditions.[3] The question of whether I or II can be observed as a stable isolated species under gas-phase conditions is of interest in understanding the rearrangement processes occurring in this potential surface. The new technique of photodissociation spectroscopy[4] provides an approach uniquely well suited to obtaining structural information about gas-phase ions, and was found to be readily applied to this case.



I II III

Experimental Section

In the photodissociation spectroscopic technique,[4] the ionic species of interest is generated and trapped in the ion cyclotron resonance cell. Under illumination by monochromatic light photodissociation of the ion may occur, and is observed by standard techniques of ion cyclotron resonance. The photodissociation cross section plotted as a function of wavelength is the photodissociation spectrum of the ion under observation, and is characteristic of the structure of the ion.[5]

In the "time resolved" photodissociation technique,[6] the photodissociation of a trapped population of ions is followed as a function of time after turning on the light source. A spectroscopically homogeneous ion population decays in smoothly exponential fashion toward the baseline; while if some of the ions are nondissociating at the given wavelength, the decay curve will tend to level off at a nonzero value. This method can clearly reveal situations where the ion population comprises two or more distinct structures.

Hexamethyl(Dewar benzene) photodissociation spectra were obtained with a pulsed ICR spectrometer technique[7] at pressure of $\sim 2 \times 10^{-8}$ Torr, ion trapping times of about 5 s, and ionizing electron energy of 30 eV. The protonated parent ion is rapidly formed by proton transfer from $(M-1)^+$ and other primary ions, and no added acid was necessary. Although the photodissociation spectrum of the parent radical cation would be of interest, no conditions were found for which the abundance of parent ion signal was greater than the expected ^{13}C isotope peak from $(M-1)^+$. Time-resolved spectra were obtained in the steady-state trapped ion ICR mode used in previous work.[8]

Spectra of protonated hexamethylbenzene were obtained with the same pulsed-ICR technique at $\sim 5 \times 10^{-8}$ Torr and 30 eV. It was necessary to add a trace of water as proton source to protonate the neutral molecule.

The absolute cross sections were obtained by reference to the known photodissociation cross section of toluene[8] at 400 nm.

Results and Discussion

Photodissociation spectra are shown in Figure 1 for both protonated hexamethylbenzene and the ion obtained by protonation of hexamethyl(Dewar benzene). (In addition to the peak shown in the figure, protonated hexamethylbenzene also showed a photodissociation peak near 285 nm having a peak cross section of the order of 1×10^{-17} cm^2. In the hexamethyl(Dewar benzene) case, the spectral region below 300 nm was obscured by extraneous photochemistry which we were unable to eliminate.) The position and intensity of the strong photodissociation peak at 385 nm is identical within experimental uncertainty for the two species, which constitutes nearly conclusive evidence for their structural identity. Since there is little doubt that the spectrum obtained for protonated hexamethylbenzene is that of structure III, it is evident that the I ions formed by initial protonation rearrange within a few seconds to III.

The homogeneity of the population of ions from protonated hexamethyl(Dewar benzene) was checked by time-resolved photodissociation at 4000 and 3700 Å, and it was found that

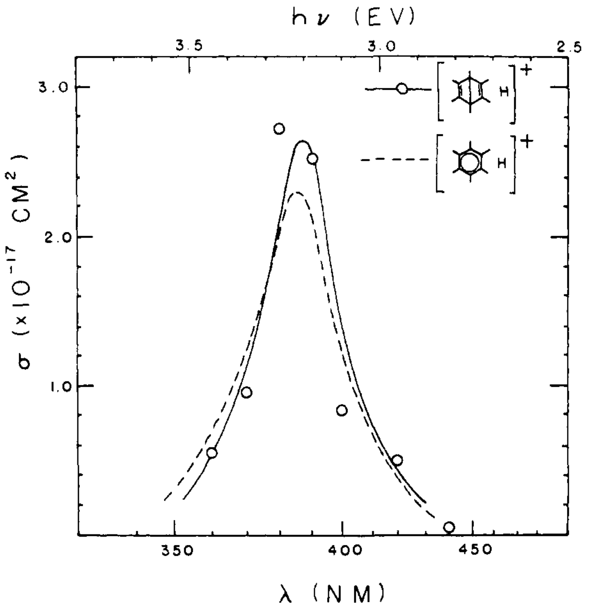


Figure 1. ICR photodissociation spectra of protonated hexamethylbenzene and protonated hexamethyl(Dewar benzene) ions.

all (>95%) of the ions dissociate uniformly, ruling out the possibility that ions of structure I or II are still present a few seconds after the initial protonation.[9]

The spectra obtained are entirely consistent with expectation for hexamethylbenzenium ion. The spectrum is very similar to the solution spectrum:[10] there is a shift of several nanometers to shorter wavelength in gas phase relative to solution. If every photon absorbed by the gas-phase ions leads to dissociation, then the photodissociation spectrum is equivalent to an optical absorption spectrum, and the gas-phase intensity is directly comparable to solution. The peak cross section of 2.3×10^{-17} cm^2 observed at 385 nm corresponds to a molar absorptivity of 6000 L/mol cm, as compared with the solution value of about[11] 6300 at 395 nm. The very close agreement between the solution absorption intensity and gas-phase photodissociation cross section provides important evidence that for this ion dissociation is the predominant fate of an excited ion, and that fluorescence or other possible competing processes are not significant.

The photodissociation spectrum of III is very similar to that obtained for protonated mesitylene by Freiser and Beauchamp[12] (although these authors do not report absolute cross sections so that no intensity comparison is possible), with the hexamethylbenzenium peaks being shifted about 30 nm to longer wavelength than those observed for 1,3,5-trimethylbenzenium ions. This red shift on adding three methyls is expected: it is similar to the red shift on going from protonated benzene to protonated mesitylene and is also analogous to the red shift in the UV spectrum on going from neutral mesitylene to neutral hexamethylbenzene. Freiser and Beauchamp[13] have discussed in detail the interpretation of the photodissociation spectra of protonated molecules, including mesitylene, in terms of excited-state acid-base properties of the neutral. These conclusions can be directly carried over to the present case; in particular it can be concluded that both the ^1L_b and ^1L_a excited states of hexamethylbenzene have greater proton affinities than the ground state. Using Freiser and Beauchamp's arguments, it can be calculated that the excited state giving the 385-nm peak in the ion, the ^1L_b state, has a proton affinity 30 kcal greater than the ground state, and the ^1L_a excited state giving the 285-nm peak in the ion has a proton affinity 28 kcal greater than the ground state. These greatly enhanced excited-state proton affinities are in line with similar enhancements observed in numerous other substituted benzene systems.[12,13] The blue shift of the spectrum relative to solution is in accord with expectation.[12]

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