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Protonated Benzene: A Case for Structural Memory Effects?[†]

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Photoionization tandem-mass spectrometry of selectively deuterium labeled precursor molecules is used to probe the structure of protonated benzene which had been questioned in a provocative publication by Mason and co-workers (*J. Chem. Soc., Chem. Commun.* **1995**, 1027). Specifically, we address the intriguing aspect of a postulated delayed hydrogen ring-walk by modulating the internal energy content of mass-selected $C_6H_{7-n}D_n^+$ ions. To this end, ionization of selectively deuterated precursors by tunable synchrotron photons is combined with chemical monitoring of H^+/D^+ transfer from $C_6H_{7-n}D_n^+$ to a strong base **B**. The resulting $\mathbf{B}H^+/\mathbf{B}D^+$ ratios monotonically decrease with increasing internal energy content and, due to the virtue of the regioselective deuterium label incorporations, thereby disprove a delayed hydrogen ring-walk or any other "structural memory effect" in $C_6H_{7-n}D_n^+$ ions. As a consequence, the experimental studies of Mason et al. were reconsidered using sector-field mass spectrometry. These extensive studies suggest that the previous observations might have been obscured by a combination of isobaric impurities, metastable-ion contributions, and artifact signals.

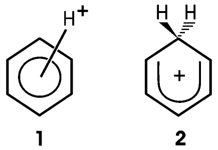
Introduction

One cannot possibly escape the warm, charming character of Professor Tom Baer, an insightful scientist and a dedicated teacher, an exemplary scholar who cares for his students. On several occasions he indicated to us that experimental findings from our laboratories had been used as teaching examples in his student courses. In this very spirit, here we would like to present a story about protonated benzene, $C_6H_7^+$, a prototype organic cation which occupies a central position in physical organic chemistry.[1]

In 1995, Mason et al.[2] published a report about an unexpected temperature dependence of the collisional activation (CA) mass spectra of protonated benzene. In brief, they found that the ratio between $H^\bullet$ and H_2 losses upon CA of mass-selected $C_6H_7^+$ depends on the temperature of the chemical ionization (CI) source used: below room temperature, loss of $H^\bullet$ prevails, whereas elimination of H_2 predominates at elevated temperatures. Moreover, for the deuterated ion $C_6HD_6^+$ generated by CI of C_6D_6 with methane, a preferential loss of $H^\bullet$ was observed at low temperatures, which was interpreted as some kind of a "memory effect" in that complete H/D equilibration does not occur. From these results, the authors concluded that the face-centered π-complex **1**, rather than the time-honored σ-complex **2** (the cyclohexadienyl cation), corresponds to the most stable structure of protonated benzene (Chart 1).

Being skeptical about this surprising result, we soon repeated the experiments. Despite our much more limited capabilities to vary the temperature of the ion source,[3] we could, however, qualitatively reproduce the effects described by Mason and co-workers. Nevertheless, doubts about Mason's assignment and conclusion remained. Radom and co-workers[4] applied high-level ab initio theory to disclaim the existence of **1**, which was identified as a second-order saddle point more than 2 eV higher in energy than **2** (which represents the global minimum). This view was further supported by several experimental and theoretical studies,[5−9] of which the spectroscopic characterizations of gaseous $C_6H_7^+$ are most impressive.[10−12] Notwithstanding, the puzzling experimental findings of Mason and co-workers persist and await an explanation.[13]

CHART 1



Here, we describe attempts to resolve matters. To this end, a specific photoionization experiment was designed in order to probe a possible memory effect in protonated benzene. In addition, the collision studies of Mason et al. were reinvestigated using sector-field mass spectrometry.

Experimental Methods

The photoionization studies were performed in the CERISES apparatus[14] installed on the beam line SA63 of the synchrotron-radiation source SuperACO at LURE (Orsay, France). This beam line has a normal incidence monochromator which provides monochromatic light in the range of 7−30 eV photon energy. Slits were at all times opened to 1 mm, corresponding to a photon-energy resolution in the range of 500 (i.e., 20 meV at 10 eV). The accuracy of the photon energy was verified by measuring the ionization energy of argon within 2 meV of its nominal value. At photon energies ≤ 11.7 eV, a LiF window was used to effectively eliminate higher order light emerging from the grating of the monochromator. The experiments without LiF filter were inherently interfered with by higher order photons and are reported without correction. Briefly, the neutral precursors introduced via a septum inlet were ionized by

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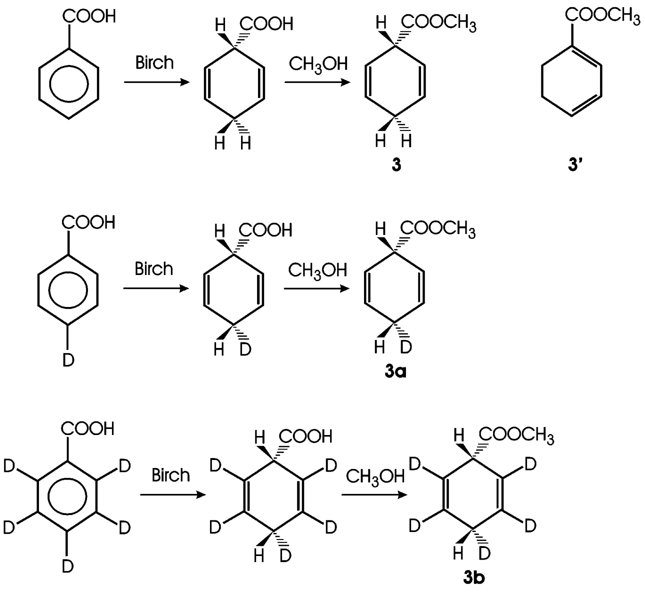
monochromatic photons, and any cations formed were extracted by a field of 1 V/cm toward a QOQ system (Q stands for quadrupole and O for octopole).[15] In the MS/MS experiments described below, Q1 was used for mass-selection of the desired $C_6H_{7-n}D_n^+$ ions. Trimethylamine as a base **B** was leaked into a reaction cell which is a 4 cm long cylinder around the octopole, and Q2 was scanned for mass analysis. The kinetic energy of the ions within the octopole was adjusted to 0.15 eV. The ion beams have Gaussian kinetic energy distributions with an average full width at half-maximum (fwhm) of ca. 0.3 eV in the laboratory frame. Ions were detected by a set of multichannel plates operating in the counting mode. The photon-energy dependences of the $\mathbf{B}H^+/\mathbf{B}D^+$ ratios were recorded in single-ion monitoring mode and are reported with corrections for the background and contributions of ^{13}C isotopes. The appearance energies reported below were determined by extrapolating the linear part of the respective single-ion monitoring curve as a function of photon energy. The given error estimates refer to these extrapolations; neither thermal contributions nor kinetic shifts were considered.

Additional experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector), which has been described elsewhere.[16] In brief, $C_6H_{7-n}D_n^+$ ions were generated by either electron ionization (EI) or chemical ionization of different precursors as detailed below. After acceleration to a kinetic energy of 8 keV, the ions of interest were mass-selected and subjected to metastable ion (MI) and collisional activation studies. MI spectra of B(1)/E(1) mass-selected ions were recorded by detection of the charged fragments formed unimolecularly in the field-free region between E(1) and B(2) by scanning the latter sector. CA spectra were recorded in the same manner using either helium (80% transmission, T) or oxygen (80% T) as stationary collision gases. In addition, MI and CA spectra were recorded in order to investigate the fragmentations occurring in other field-free regions of the Berlin mass spectrometer using the following methods:[17,18] (i) direct analysis of the daughter ions (DADI) formed in the field-free region between the ion source and the first magnet by means of a linked B(1)/E(1) scan and (ii) mass selection of $C_6H_{7-n}D_n^+$ with B(1) only and recording the fragmentations occurring in the field-free region between B(1) and E(1) by scanning the latter (MIKE scan). The kinetic energy of the ionizing electrons was varied by adjusting the voltage between the filament and the source with the repeller grounded to the source; the latter is important in order to avoid unintentional acceleration of the electrons entering the source toward the repeller.[3] The ionization energy of benzene (IE = 9.24 eV) was used as an anchor for the electron-energy scale. Note, however, that the electrons evolving from the hot filament are not at all monoenergetic, and the dependence reported below is largely meant qualitatively. Further, MI and CA spectra were recorded at different temperatures of the ion source. Because the ion source is usually heated to 200 °C and not equipped with a cooling device, these experiments were performed as follows. 12 h prior to the actual measurements, the ion optics were optimized first and the source heater was switched off, to allow the source to reach ambient temperature. Then, the precursors were introduced, and spectra were immediately recorded while monitoring the source temperature, which increases continuously due to the heat emitted by the glowing filament. In about a half-hour, the source reaches ca. 160 °C, and higher temperatures were achieved by additional heating. In general, CA spectra recorded in a sector instrument are a superposition of collision-induced fragmentations occurring in the collision cell and unimolecular processes occurring in the entire field-free region. Due to the particularly long third field-free region of the Berlin BEBE instrument (1.9 m), the contribution of metastable ions to the CA spectra is quite pronounced. The CA spectra can be corrected for MI contributions by monitoring the absolute signals at a fixed multiplier voltage as well as the parent ion transmission in MI and CA experiments conducted directly after each other, thereby allowing one to subtract the MI components from the CA spectra.

SCHEME 1

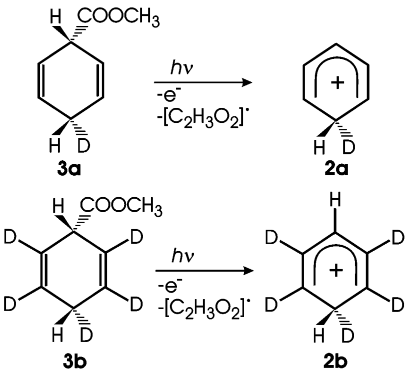


The carboxymethyl cyclohexa-2,5-dienes **3**, **3a**, and **3b** were prepared by Birch reduction of the corresponding benzoic acids followed by esterification with methanol (Scheme 1).[19] The compounds were purified by bulb-to-bulb distillation (20 mbar) and characterized by ^1H NMR and GC-MS. In the course of the synthesis, 5−10% of the corresponding conjugated carboxymethyl cyclohexa-1,3-dienes (e.g., **3′**) are formed, probably via proton catalysis in the course of esterification. In addition, the samples undergo transfer hydrogenation as well as autoxidation during storage and thus contain some of the corresponding methyl benzoates as well as traces of carboxymethyl cyclohexenes.[20] Unfortunately, further purification of the samples by means of preparative gas chromatography is hampered by dehydrogenation to methyl benzoate occurring in the heated inlet block. Notwithstanding, these impurities do not affect the qualitative outcome of the photoionization experiments described below.

Results and Discussion

One option for rationalizing the findings of Mason et al.[2] without shaking the fundaments of physical organic chemistry is that the hydrogen ring-walk[21] in protonated benzene is not that fast as usually anticipated when the internal energy content of structure **2** is sufficiently low. Upon reacting with a base **B**, such a “cold” ion **2** is expected to preferentially transfer one of the hydrogens of the methylene group. Only if hydrogen ring-walk is fast, all hydrogen atoms are equilibrated. According to experiment and theory, the barrier for hydrogen ring-walk is on the order of 0.27−0.45 eV.[4,8,22−25] Although it would be somewhat surprising that a barrier of this height is not surmounted in the experiment, it could be argued that at the low temperatures achievable in the apparatus of Mason et al.

SCHEME 2



(T_{min} = 213 K) in conjunction with sampling the ions within about a microsecond, some of the $C_6H_{7-n}D_n^+$ ions have not undergone complete H/D equilibration via the ring-walk mechanism. Upon collisional activation, the H(D) atoms of the methylene group may then be lost preferentially. Following this scenario, dissociative ionization of the selectively deuterated precursors **3a** and **3b** concomitant with loss of neutral $[C_2H_3O_2]$ [26] could provide access to the specifically labeled cyclohexadienyl cations **2a** and **2b** (Scheme 2). Note that the choice of the precursors is in close analogy to previous studies of Kuck, Grützmacher, and co-workers.[21,27−29]

Another important aspect needs to be addressed right at the outset. Potentially, there exist numerous isomeric structures of $C_6H_7^+$, e.g., acyclic ones, fulvenes, and systems with bicyclic skeletons.[7,24] However, a consideration of the experimental conditions in the work of Mason et al.[2] implies that an internally consistent explanation of the observed effects would indeed require an isomer of protonated benzene which is *more stable* than structure **2**. Specifically, it needs to account for the anomalies in the $H^\bullet$ and $D^\bullet$ losses, which were observed at lowest temperatures, and the fact that the collision experiments sample the entire population of ions, rather than just a minor fraction of isomeric species. As Mason et al. used benzene as the neutral precursor in their chemical ionization studies, any high-energy isomers (e.g., protonated fulvene),[7] even if they might be formed in small amounts, cannot explain the changes of the gross population of ions. With respect to the unique thermochemical stability of benzene among the 217 possible C_6H_6 isomers,[30] we therefore restrict ourselves to consideration of structures **1** and **2**.[31]

Photoionization Experiments. In analogy to a previous study on the titration of the barrier for the keto/enol tautomerization in ionized acetamide,[32] the photoionization experiments were designed as follows. The neutral samples **3**, **3a**, and **3b**, respectively, were introduced into the ion source and ionized with photons from tunable synchrotron radiation; the ions of interest, $C_6H_7^+$ for **3**, $C_6H_6D^+$ for **3a**, and $C_6H_2D_5^+$ for **3b**, were mass-selected using the quadrupole Q1 and interacted with a base **B** in the octopole ion guide at near thermal energy (E_{lab} = 0.15 eV); and the ratio of the proton-transfer products **B**H^+ and **B**D^+ was monitored using the second mass analyzer Q2. The key variable is the energy of the ionizing photons, while all other parameters are kept constant. The intention of this kind of experiment is to vary the internal energy content of the reactant ion by tuning the photon energy and to probe possible consequences (if there are any) in a chemical reaction which serves as a monitor.[32] While this approach is quite straightforward for photoionization to a molecular cation, the present experiment should also probe whether the idea of the "titration method" can be transferred to a fragment ion formed in dissociative photoionization. In addition, one should note that the internal energy of the fragment ion does not correspond directly to the difference of the photon energy and the threshold for dissociative photoionization, but to a somewhat lower amount because some energy may be lost in both the leaving electron and the neutral fragment formed; we return to this aspect in more detail further below. A control of the ions' internal energy by means of coincidence methods is generally conceivable but less well-defined for fragments formed upon dissociative ionization and is moreover likely to be associated with a rather poor sensitivity.

The choice of the base is critical in the present experiment. If the proton affinity of the base PA(**B**) is smaller than PA(benzene), proton transfer is unlikely to occur at all. If PA(**B**) ≈ PA(benzene), that is, proton transfer is more or less thermoneutral, formation of a long-lived ion/neutral complex (INC)[33] is likely to occur in which reversible processes might hide the structural information introduced by the regioselective isotopic labeling of the precursors.[19] Similar considerations apply for slightly exothermic proton transfer, PA(**B**) > PA(benzene). Only a considerably exothermic proton transfer, PA(**B**) ≫ PA(benzene), whose exothermicity exceeds the typical binding energies of INCs (up to 1 eV), could lead to immediate H^+ or D^+ transfer without involving long-lived intermediates. Moreover, the base should not contain exchangeable protons itself because secondary reactions may otherwise lead to H/D exchange reactions and might thus deplete the **B**D^+ signal. Given PA(benzene) = 7.78 eV, trimethylamine (PA = 9.84 eV)[34] was therefore considered an appropriate reagent serving as base **B**.

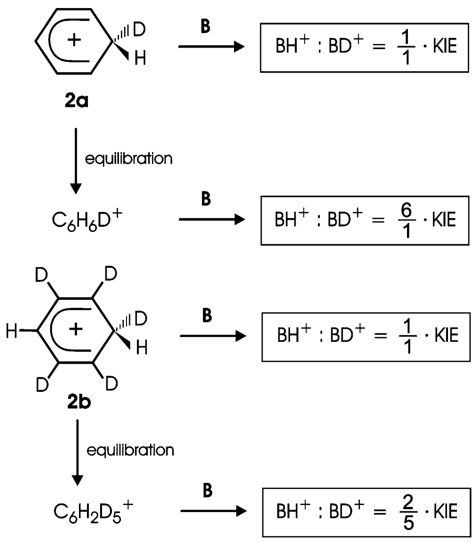
$$C_6H_7^+ + (CH_3)_3N \rightarrow (CH_3)_3NH^+ + C_6H_6 \qquad (1)$$

When interacting mass-selected $C_6H_7^+$, generated by dissociative photoionization of **3**, with trimethylamine under the conditions described above, proton transfer is observed exclusively (reaction 1). Two additional ionic products, the radical cation $(CH_3)_3N^{\bullet+}$ and the immonium ion $(CH_3)_2NCH_2^+$, are observed at low photon energies and can be traced back to an isobaric interference of mass-selected $C_6H_7^+$ with the $^{13}C_1$-isotope of $C_6H_6^{\bullet+}$ co-generated upon dissociative photoionization of **3**. Accordingly, these products are not pursued any further (but were included in the isotope correction of the $(CH_3)_3NH^+$ signals).

Before presenting the experimental findings, we address the concept of the present experiments in some more detail. Irrespective of the actual structure of the $C_6H_{7-n}D_n^+$ ions, H^+ or D^+ transfer to a base **B** might be associated with a kinetic isotope effect (KIE), which itself depends on the internal energy of the $C_6H_{7-n}D_n^+$ ions and can generally be expected to decrease with increasing energy content.[35] Furthermore, in the case of complete H/D equilibration occurring before the ions enter the reaction region, the different numbers of H and D atoms in the reactant ions have to be acknowledged by statistical corrections. If, however, the $C_6H_{7-n}D_n^+$ ions "remember" their origin from the selectively labeled neutral precursors **3a** and **3b**, respectively, that is, if hydrogen ring-walk is slow at low internal energies, both ions **2a** and **2b** will bear a 1:1 ratio of H^+ and D^+ transfer modified by a KIE (Scheme 3).[36,37]

Given the generally valid assumption that apparent KIEs decrease with increasing internal energy[35] and that rapid H/D equilibration of $C_6H_{7-n}D_n^+$ takes place at elevated energies, the present experiments allow for qualitative distinction of the structural effects (i.e., delayed hydrogen ring-walk) and KIEs (Figure 1). If the specifically labeled ions **2a** and **2b** are formed

SCHEME 3



at low energies, the **B**H$^+$/**B**D$^+$ ratios of both ions should start from a common value and then diverge to approach the respective KIE-modified statistical limits at larger energies due to H/D equilibration (case a); these limits are **B**H$^+$/**B**D$^+$ = (6/1)KIE for $C_6H_6D^+$ generated from **3a** and **B**H$^+$/**B**D$^+$ = (2/5)KIE for $C_6H_2D_5^+$ generated from **3b**. If instead hydrogen ring-walk is rapid, the variation of the **B**H$^+$/**B**D$^+$ ratios should qualitatively show the same energy behavior with an offset due to the different number of H and D atoms in the ions **2a** and **2b** (case b). Accordingly, it is not the precise values of the **B**H$^+$/**B**D$^+$ ratios but merely the qualitative inspection of the trends as a function of the energy of the ionizing photons that should reveal whether any kind of structural memory exists in protonated benzene. There is, of course, a third alternative in that the dissociative photoionization of the neutral precursors itself already deposits too much internal energy in the $C_6H_{7-n}D_n^+$ ions formed such that no distinct energy dependence of the **B**H$^+$/**B**D$^+$ ratios is obtained (case c); this may in fact be true in many cases of dissociative ionization, but fortunately does not apply here. Further, while KIE in a proton-transfer reaction certainly depends on the base **B**, this effect would only influence the actual values of the **B**H$^+$/**B**D$^+$ ratios in the experiments but not change the qualitative difference of the trends. Finally, to avoid a misleading interpretation of the graphs, note the deviation of this kind of "gas-phase titration"[32] from threshold collision-induced dissociation and related experiments. In the present study, the interaction energy of the ions and the neutral reagent is kept constant throughout the experiments, while only the "history" of the reactant ions is changed by variation of the energy of the ionizing photons.

After this more general consideration of the experiment, we also need to comment briefly on the purity of the samples. According to GC-MS and ^{1}H NMR analysis, in addition to the desired compounds **3**−**3b**, the samples contain 5−10% of the corresponding carboxymethyl cyclohexa-1,3-dienes (**3′**−**3b′**) and ca. 5% of methyl benzoate. The latter impurity does not matter in the present MS/MS experiments because dissociative ionization of methyl benzoate does not yield $C_6H_7^+$. As confirmed by their EI mass spectra, the isomeric conjugated dienes **3′**−**3b′**, however, also yield $C_6H_{7-n}D_n^+$ ions upon photoionization (though in lower yields, as implied by a comparison of the EI mass spectra of **3** and **3′**).[38] Thus, a certain fraction of the $C_6H_{7-n}D_n^+$ species will have a different origin. Nevertheless, with **3**−**3b** as the major components of the neutral samples, the impurities due to the conjugated dienes should not disturb the qualitative trends in the energy dependence of the monitoring reaction (cases a−c in Figure 1).

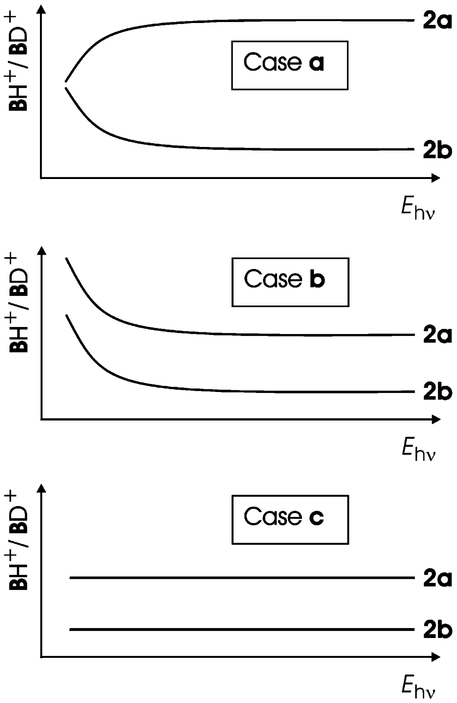


Figure 1. Qualitative sketches of the different **B**H$^+$/**B**D$^+$ ratios expected in the photoionization experiments. See text for details.

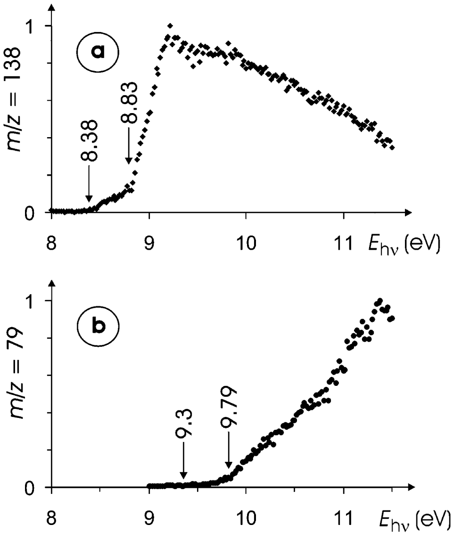


Figure 2. Single-ion monitoring of (a) $m/z = 138$ (parent ion) and (b) $m/z = 79$ ($C_6H_7^+$) as a function of photon energy (eV). The appearance energies referred to in the text are derived from extrapolation of the linear part of the thresholds to the baseline without applying any further corrections.

As a consequence of the impurity of the samples, the parent ion shows a composite appearance curve (Figure 2a). Of the two photoionization thresholds, the lower, minor one is assigned as AE($3'^{+}$) = 8.38 ± 0.04 eV and the higher, major component as AE(3^+) = 8.83 ± 0.03 eV. Here, the assignment is not only based on the composition of the sample with **3** as the leading component but also on a comparison with the corresponding parent compounds. Thus, the ionization energy (IE) of 1,3-cyclohexadiene amounts to 8.25 ± 0.02 eV, whereas that of 1,4-cyclohexadiene (8.82 ± 0.02 eV) is significantly larger.[39] A slight increase of the IE for **3′** is fully consistent with

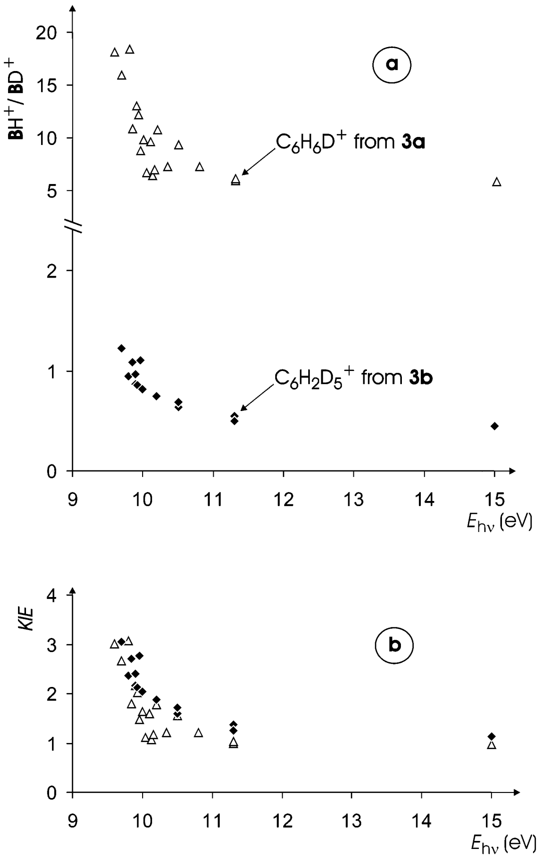


Figure 3. (a) **B**H^+/**B**D^+ ratios in the ion/molecule reactions of trimethylamine with mass-selected $C_6H_6D^+$ (from **3a**, ▲) and $C_6H_2D_5^+$ (from **3b**, ♦), respectively, as a function of the energy of the ionizing photons. (b) Same **B**H^+/**B**D^+ ratios as a function of photon energy after statistical correction for the number of H and D atoms in the mass-selected $C_6H_{7-n}D_n^+$ ions.

substitution of the conjugated diene with an electron-accepting ester group. Instead, the presence of a carboxymethyl group in one of the allylic positions of 1,4-cyclohexadiene hardly affects the IE. Like the parent ions, also the $C_6H_7^+$ ions emerging from dissociative photoionization show a composite threshold behavior with a tentative AE($C_6H_7^+$) = 9.3 eV for the first, minor component smoothly rising out of the noise level and AE($C_6H_7^+$) = 9.79 ± 0.05 eV for the second, larger one (Figure 2b). By analogy, these two thresholds are assigned to dissociative photoionization of **3′** and **3**, respectively, with **3** giving rise to the major component having the larger AE. As stated above, the presence of the isomeric dienes **3a′** and **3b′** in the respective neutral samples may somewhat modify the quantitative outcome of the monitor reactions of the labeled ions, while the qualitative behavior should not be affected; this is all that matters in the present context. We conclude this description by noting that the measured AE = 9.29 ± 0.04 eV for ionized methyl benzoate agrees reasonably well with the literature value of 9.32 ± 0.04 eV.[39]

As expected, the $C_6H_{7-n}D_n^+$ ions generated from the labeled samples **3a** and **3b** undergo H^+ and D^+ transfers with trimethylamine. With increasing photon energy, the **B**H^+/**B**D^+ ratios rapidly decrease for both labeled precursors (Figure 3a). Despite considerable scatter at low photon energies, two important pieces of information can be extracted directly from the graph. First, a clear energy behavior is observed, thus confirming the validity of the experimental approach in that variation of the energy of the ionizing photons does indeed markedly affect the internal energy content of mass-selected fragment ions formed upon dissociative photoionization. Second, the trends quite clearly follow the scenario of case b in Figure 1. Thus, even an experiment which was especially designed to probe the possible existence of a "memory effect" in the H/D distribution of protonated benzene fails to provide any evidence of such an effect. Instead, the experiments clearly demonstrate complete H/D equilibration of the mass-selected $C_6H_{7-n}D_n^+$ ions; thus, a rapid hydrogen ring-walk takes place on the time scale of the experiment. Accordingly, we can compare the **B**H^+/**B**D^+ ratios of the different precursor ions after statistical correction for the deuterium content (Figure 3b). At low energies of the ionizing photons and thus low internal energy content of the $C_6H_{7-n}D_n^+$ ions, a KIE on the order of 3 is observed for both ions made from **3a** and **3b**, respectively, which then rapidly decreases, approaching a limiting value of KIE = 1 at elevated photon energies. The significant KIEs at low internal energies are fully consistent with previous studies of the thermal ion/molecule reactions of $C_6H_{7-n}D_n^+$ with various bases in which KIEs between 1.2 and 5.7 were found, dependent on the base **B** used.[5,6] Likewise, the almost vanishing KIE at higher photon energies agrees with the finding that the unimolecular loss of dihydrogen from $C_6H_{7-n}D_n^+$ ions (reaction 2) is associated with an almost statistical H/D distribution in the product ions.[6,28]

$$C_6H_7^+ \rightarrow C_6H_5^+ + H_2 \qquad (2)$$

From a methodological point of view, we note that the increasing internal energy content of the mass-selected $C_6H_{7-n}D_n^+$ ions is also implied by the observation of unimolecular dehydrogenation according to reaction 2 in the absence of a reactant gas in the octopole. The apparent threshold for the unimolecular decay of mass-selected $C_6H_7^+$ to $C_6H_5^+$ is about 13.3 ± 0.2 eV and thus ca. 3.5 eV above AE($C_6H_7^+$) = 9.79 ± 0.05 eV. These observations can be used to roughly estimate the energy partitioning in dissociative photoionization of **3**. As the thermodynamic threshold of reaction 2 amounts to 2.79 eV and it occurs without an appreciable barrier in excess of the reaction endothermicity,[7] we can conclude that up to about four-fifths of the excess energy of the ionizing photons can be deposited as internal energy in the photofragment $C_6H_7^+$.[40]

Sector-Field Mass Spectrometry. The photoionization experiments described above demonstrate that at least the hypothesis of a significantly delayed hydrogen ring-walk cannot account for the anomalies reported by Mason and co-workers.[2] In addition, none of the many other studies on this topic[4−13,24] has so far provided even a hint of evidence for a low-energy structure other than **2**, which could account for their findings.

As stated in the Introduction, quite soon after Mason's publication we qualitatively reproduced the reported effect in that collisional activation of $C_6HD_6^+$, produced by CI of C_6D_6 with CH_4, shows a temperature dependence in the hydrogen losses with expulsion of $H^•$ being preferred at low ion-source temperature. While the effect turned out to be much smaller in our experiments than reported by Mason et al., a qualitative agreement was nevertheless achieved. We thus presumed to have confirmed their findings and ascribed the quantitative difference (much smaller effect) to our limited capability to control the temperature of the ion source.[3] However, in view of the mounting evidence against protonated benzene having structure other than **2**, we decided to carefully reconsider the sector-field studies. Of the many experiments having been performed with different precursors (benzene, 1,4-cyclohexadiene, and **3**−**3b**) and various ionization methods (EI and CI at different temperatures of the ion source and variable kinetic energies of the

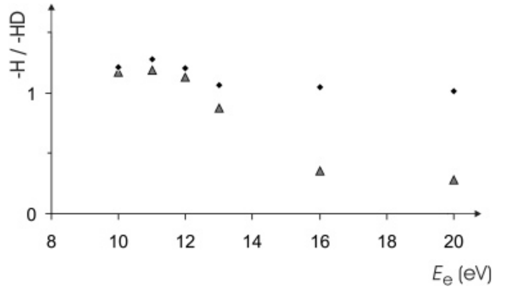


Figure 4. Ratio of $H^\bullet$ and HD losses in the CA spectra (He, 80% T) of B(1)/E(1) mass-selected $C_6H_6D^+$ ions (from **3a**) as a function of the kinetic energy of the ionizing electrons without (▲) and with (♦) correction for contributions of metastable ions. See text for details.

ionizing electrons), we select just two cases here to illustrate the various kinds of effects being operative.

The first experiment to be described starts with dissociative EI of neutral **3a**, followed by mass selection of $C_6H_6D^+$ using B(1)/E(1), collisional activation (He, 80% T) in the field-free region between E(1) and B(2), and analysis of the fragment ions with B(2). Here, the variable is the energy of the ionizing electrons in the range from 10 to 20 eV. As a representative parameter, we have chosen the ratio of $H^\bullet$ and HD losses (in $\Delta m = -2$, losses of isobaric $D^\bullet$ and H_2 cannot be resolved). The raw data (▲ in Figure 4) do indeed show a dependence on the kinetic energy of the ionizing electrons, which is in qualitative agreement with the effect described in ref 2 (less $H^\bullet$ loss at elevated energies). However, it needs to be acknowledged that every CA spectrum recorded in a sector-field mass spectrometer is a superposition of fragmentations due to unimolecular decay taking place in the entire field-free region and collision-induced dissociation occurring in the collision cell only. This is particularly true for the unusually long (1.9 m) third field-free region of the Berlin BEBE instrument.[16] Metastable $C_6H_7^+$ only undergoes loss of H_2, whereas collisional activation leads to an additional expulsion of $H^\bullet$. The MI contribution to the CA spectrum will thus appear as an overestimation of the H_2 channel. A correction for the MI contributions can be made by consideration of the total ion currents, and doing so, the temperature effect vanishes within the scatter of the experimental data obtained at different temperatures of the ion source (♦ in Figure 4). A simple rationale for this phenomenon is that the fraction of metastable ions in the beam increases at elevated energies of the ionizing electrons. Nevertheless, it may be argued that dissociative EI of **3a** already is too energetic such that the temperature dependence described by Mason et al. might not be probed adequately in this way.

Figure 5 shows the fraction of $H^\bullet$ losses[41] upon CA (O_2, 80% T) of $C_6H_7^+$ generated by dissociative EI of 1,4-cyclohexadiene as a function of the temperature of the ion source. In a linked B(1)/E(1) scan (DADI, ▲ in Figure 5), a clear temperature dependence is observed with decreasing $H^\bullet$ loss at elevated temperatures, which is in qualitative agreement with the observation of Mason et al. The CA spectra of B(1)/ E(1) mass-selected $C_6H_7^+$ (♦ in Figure 5) show somewhat lower amounts of $H^\bullet$ losses, but a slight decrease of this channel with increasing temperature of the ion source can still be observed; the lower fraction of $H^\bullet$ loss compared to the linked-scan experiment is again due to the superimposed MI processes. If, however, the contributions of metastable ions to the CA spectra are corrected for, the temperature dependence disappears within the scatter of the data (■ in Figure 5). Thus, much like the electron energy (Figure 4), the temperature of the ion source appears to increase the fraction of metastable ions in the $C_6H_7^+$ ion beam. The more pronounced effect in the DADI experiments may also have other origins (see below).

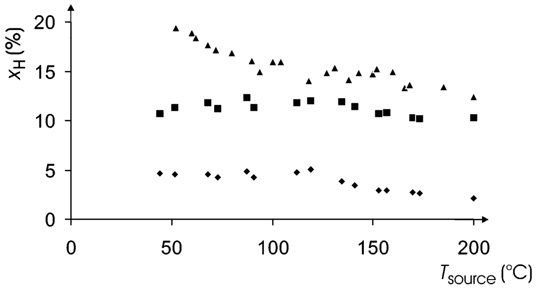


Figure 5. Fraction of $H^\bullet$ loss[41] in the CA spectra (O_2, 80% T) of $C_6H_7^+$ recorded in a B/E linked scan (▲) and of B(1)/E(1) mass-selected $C_6H_7^+$ without (♦) and with (■) correction for contributions of metastable ions to the CA spectra as a function of the temperature of the CI source. The $C_6H_7^+$ ions were generated by dissociative EI of 1,4-cyclohexadiene.

As far as chemical ionization of benzene with methane as reagent gas is concerned, it turned out essential to carefully monitor the $C_6H_6^{\bullet+}/C_6H_7^+$ ratio during the experiments because the $^{13}C_1$-isotope of ionized benzene interferes with the protonated form. As loss of $H^\bullet$ forms the base peak in the CA mass spectrum of mass-selected $C_6H_6^{\bullet+}$, any contribution of $^{13}C_1-C_6H_6^{\bullet+}$ would give rise to an increase of the $H^\bullet$ channel. At least in our instrument, changing the temperature of the ion source also affects the CI conditions, the $C_6H_6^{\bullet+}/C_6H_7^+$ ratio varies as well, and so does the branching between $H^\bullet$ and H_2 losses. In fact, all we can extract from the various CI experiments having been performed with B(1)/E(1) mass-selected $C_6H_{7-n}D_n^+$ ions is that we obtained no obvious evidence for a temperature dependence of the CA spectra of $C_6H_7^+$ which cannot be attributed to either metastable ion contributions or isobaric interferences.

Finally, it needs to be commented on the fact that Mason et al. recorded the CA spectra of $C_6H_7^+$ using a linked-scan technique in a two-sector instrument. Upon reinvestigation of these experiments with the BE front-end of our mass spectrometer, significant artifact signals are found to appear in the region of hydrogen losses in both kinds of MI experiments possible with two sectors only (DADI and MIKE spectra; see experimental details).[17] For example, signals at $\Delta m = -1$ can reach up to about 20% in DADI and MIKE experiments, whereas the abundance of unimolecular $H^\bullet$ loss is well below 1% of the H_2 loss for B(1)/E(1) mass-selected $C_6H_7^+$. This difference is due to artifact signals in the DADI and MIKE experiments which can arise from various fragment ions, isotopologs, or minor other products formed in the CI plasma. Dependent on the scanning techniques used and the respective configuration of the instrument, these artifacts may severely obscure the MI spectra.[17,42,43] In addition, we note that the amounts of MI and CA contributions in the DADI experiments are also affected by the CI conditions because fragmentation is sampled in a field-free region spatially close to the ionization volume such that the pressure of the collision gas(es) may vary.

Conclusions

Previous spectroscopic studies in the gas phase have demonstrated that protonated benzene has the structure of the σ-complex **2**.[10−12] The present photoionization experiments with mass-selected $C_6H_{7-n}D_n^+$ ions intend to address a possible memory effect as far as the labeling distribution is concerned. The results obtained demonstrate that the photon energy does indeed have an effect on the $\mathbf{B}H^+/\mathbf{B}D^+$ ratios, thus proving the validity of the experimental approach. The qualitative trends observed are fully consistent with a behavior that is typical for the σ-complex **2**. Provided the reasonable assumption holds true that the precursor compounds used here yield specifically labeled $C_6H_{7-n}D_n^+$ ions upon dissociative photoionization near threshold, we can conclude that all H and D atoms in $C_6H_{7-n}D_n^+$ are completely equilibrated at ambient temperature. This finding is fully consistent with a low barrier associated with hydrogen ring-walk (about 0.35 eV).[21] None of the experiments provides evidence for a delayed hydrogen ring-walk or a structural memory effect, not to speak of the existence of the π-complex **1**.

According to our additional experiments with a sector-field mass spectrometer, the surprising results of Mason et al. are likely to be due to the combined action of artifact signals, isobaric interferences, and metastable ion contributions to the collisional activation spectra. While we frankly admit that our capabilities to vary the temperature of the ion source are limited compared to the equipment used in ref 2, with the present knowledge it appears that the evidence presented by Mason et al. in favor of a face-centered π-complex of benzene was in fact inconclusive.[44]

From a methodological point of view, the present photoionization experiments demonstrate that the gas-phase titration method developed for the determination of the barrier of the keto/enol tautomerization of ionized acetamide[32] can also be applied to fragment ions generated by dissociative photoionization.

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References and Notes

(1) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 2001.

(2) Mason, R. S.; Williams, C. M.; Anderson, P. D. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1027.

(3) Schröder, D.; Loos, L.; Semialjac, M.; Weiske, T.; Schwarz, H.; Höhne, G.; Thissen, R.; Dutuit, O. *Int. J. Mass Spectrom.* **2002**, *214*, 155.

(4) Glukhovtsev, M. N.; Pross, A.; Nicolaides, A.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1995**, 2347.

(5) Chiavarino, B.; Crestoni, M. E.; DePuy, C. H.; Fornarini, S.; Gareyev, R. *J. Phys. Chem.* **1996**, *100*, 16201.

(6) DePuy, C. H.; Gareyev, R.; Fornarini, S. *Int. J. Mass Spectrom.* **1997**, *161*, 41.

(7) Bouchoux, G.; Yáñez, M.; Mó, O. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 241.

(8) Ascenzi, D.; Bassi, D.; Franceschi, P.; Tosi, P.; Di Stefano, M.; Rosi, M.; Sgamellotti, A. *J. Chem. Phys.* **2003**, *119*, 8366.

(9) See also: Reed, C.; Kim, K.-C.; Stoyanov, E. S.; Stasko, D.; Tham, F. S.; Mueller, L. J.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2003**, *125*, 1796.

(10) Solca, N.; Dopfer, O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3628.

(11) Jones, W.; Boissel, P.; Chiavarino, B.; Crestoni, M. E.; Fornarini, S.; Lemaire, J.; Maitre, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 2057.

(12) Solca, N.; Dopfer, O. *Chem. Eur. J.* **2003**, *9*, 3154.

(13) See also: Kryachko, E. S.; Nguyen, M. T. *J. Phys. Chem. A* **2001**, *105*, 153.

(14) Dutuit; O.; Alcaraz, C.; Gerlich, D.; Guyon, P. M.; Hepburn, J. W.; Metayer-Zeitoun, C.; Ozenne, J. B.; Weng, T. *Chem. Phys.* **1996**, *209*, 177.

(15) Franceschi, P.; Thissen, R.; Žabka, J.; Roithová, J.; Herman, Ž.; Dutuit, O. *Int. J. Mass Spectrom.* **2003**, *228*, 507.

(16) Schalley, C. A.; Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 173.

(17) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry: Techniques and Applications of Tandem Mass Spectrometry*; VCH: Weinheim, Germany, 1988.

(18) Schröder, D.; Oref, I.; Hrušák, J.; Weiske, T.; Nikitin, E. E.; Zummack, W.; Schwarz, H. *J. Phys. Chem. A* **1999**, *103*, 4609.

(19) In the schemes, we designate only one particular stereoisomer of the Birch-reduction products for the sake of clarity. In practice, however, the Birch reaction occurs without a particular diastereoselectivity; see ref 1, p 1010.

(20) According to the photoionization mass spectra acquired in Orsay, the unlabeled sample of **3** showed an increased content of methyl benzoate, which we assign to autoxidation during transportation from the Berlin laboratory where the compounds were prepared.

(21) Kuck, D. *Int. J. Mass Spectrom.* **2002**, *213*, 101.

(22) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 6299.

(23) Cacace, F.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1992**, *114*, 6776.

(24) Sumathy, R.; Kryachko, E. S. *J. Phys. Chem. A* **2002**, *106*, 510.

(25) In ref 21, the barrier is given with even larger accuracy, 0.35 ± 0.01 eV.

(26) For details of the $[C_2H_3O_2]$ system, see: Schröder, D.; Semialjac, M.; Schwarz, H. *Eur. J. Mass Spectrom.* **2003**, *9*, 287, and references therein.

(27) Kuck, D.; Bather, W.; Grützmacher, H.-F. *J. Am. Chem. Soc.* **1979**, *101*, 7154.

(28) Kuck, D.; Schneider, J.; Grützmacher, H.-F. *J. Chem. Soc., Perkin Trans. 2* **1985**, 689.

(29) Mormann, M.; Kuck, D. *Int. J. Mass Spectrom.* **2002**, *219*, 497.

(30) Bock, H. *Angew. Chem.* **1989**, *101*, 1659; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1627.

(31) For a similar situation in the related $C_6H_6^{\bullet+}$ system, see: Baer, T.; Willett, G. D.; Smith, D.; Phillips, J. S. *J. Chem. Phys.* **1979**, *70*, 4076.

(32) Schröder, D.; Loos, J.; Schwarz, H.; Thissen, R.; Dutuit, O.; Mourgues, P.; Audier, H.-E. *Angew. Chem.* **2002**, *114*, 2867; *Angew. Chem., Int. Ed.* **2002**, *41*, 2748.

(33) McAdoo, D. J.; Morton, T. H. *Acc. Chem. Res.* **1993**, *26*, 295.

(34) All proton affinities are taken from: Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(35) For a more detailed discussion of KIEs, see: Derrick, P. J.; Donchi, K. F. in *Comprehensive Chemical Kinetics*, Vol. 24; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1983; p 53.

(36) To a first approximation, secondary KIEs are neglected.

(37) Note that the spectroscopic studies of gaseous $C_6H_7^+$ ions clearly reveal structure **2** but cannot address the question of a delayed hydrogen-ring walk.

(38) MS (EI, 70 eV) of **3**, *m/z* (%): 138 (4) $[M^+]$, 137 (4) $[M^+ - H]$, 107 (4) $[M^+ - CH_3O]$, 79 (100) $[C_6H_7^+]$, 78 (45) $[C_6H_6^+]$, 77 (55) $[C_6H_5^+]$, 59 (5) $[C_2H_3O_2^+]$, and 51 (8) $[C_4H_3^+]$. MS (EI, 70 eV) of **3′**, *m/z* (%): 138 (50) $[M^+]$, 137 (60) $[M^+ - H]$, 107 (35) $[M^+ - CH_3O]$, 79 (100) $[C_6H_7^+]$, 78 (30) $[C_6H_6^+]$, 77 (95) $[C_6H_5^+]$, 59 (10) $[C_2H_3O_2^+]$, and 51 (15) $[C_4H_3^+]$.

(39) Unless mentioned otherwise, all data are taken from the NIST Standard Reference Database No. 69, March 2003 Release; see: http://webbook.nist.gov/chemistry/.

(40) See also: Murray, P. T.; Baer, T. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *30*, 165.

(41) Normalized to the sum of $H^\bullet$ and H_2 losses; i.e., $x_H = I([M - H]^+)/(I([M - H]^+) + I([M - H_2]^+))$.

(42) Boyd, R. K.; Porter, C. J.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *44*, 199, and references therein.

(43) See also: (a) Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1995**, *146/147*, 183. (b) Mouget, Y.; Bertrand, M. J. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 387.

(44) Maddox, J. *Nature* **1994**, *369*, 97.