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Hydrogen atom elimination from polycyclic aromatic hydrocarbons with sustained off-resonance irradiation: a new approach to produce carbon/hydrogen cluster cations $C_nH_x^+$

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Abstract

The stepwise elimination of hydrogen atoms from nine polycyclic aromatic hydrocarbons (PAHs) was investigated by the collision-induced dissociation of the sustained off-resonance irradiation (SORI-CID) technique of Fourier transform ion cyclotron resonance mass spectrometry. In every case the application of sequential SORI-CID resulted in the predominant loss of a single hydrogen atom from the parent ions, and for coronene, perylene, and benz[a]anthracene, this eventually produced pure carbon cluster ions $C_n^{\cdot+}$. No carbon cluster ions were observed for small PAHs because of competing fragmentations or insufficient intensities of the parent ions. As a common feature of the larger polycyclic aromatic hydrocarbons studied, hydrogenated carbon cluster ions $C_nH_5^+$ were produced smoothly after elimination of five hydrogen atoms (from pyrene, $C_{16}H_{10}$, and fluorene, $C_{13}H_{10}$) or of seven hydrogen atoms (from coronene, $C_{24}H_{12}$, perylene, $C_{20}H_{12}$, benz[a]anthracene, $C_{18}H_{12}$, chrysene, $C_{18}H_{12}$, and triphenylene, $C_{18}H_{12}$). However, uncomplicated further loss of hydrogen atoms to produce cluster ions $C_nH_4^{\cdot+}$ (or $C_nH_3^+$) was observed only for benz[a]anthracene, chrysene, and triphenylene. The different dissociations of $C_nH_x^+$ with odd and even numbers of hydrogen atoms and the difficulty to form $C_nH_x^+$ ($0 \leq x \leq 4$) by multisteps of single hydrogen elimination are discussed. The latter observation may be attributed to characteristically different structures of hydrogenated carbon cluster ions $C_nH_x^+$ with $x \geq 5$ and $x \leq 4$. (Int J Mass Spectrom 185/186/187 (1999) 1–10) © 1999 Elsevier Science B.V.

Keywords: Sustained off-resonance irradiation (SORI); Collision-induced dissociation (CID); Hydrogen elimination; Polycyclic aromatic hydrocarbon; Carbon cluster

1. Introduction

For decades carbon clusters have been the subject of intense research efforts [1], which has led the way to the discovery and the successful study of the fullerenes [2]. The synthesis of macroscopic quantities of fullerenes, such as C_{60}, C_{70}, C_{76}, C_{84}, and so on, has resulted in prospects of potential applications of fullerene based materials. As for the formation of small carbon clusters with ≤30 atoms, high frequency spark evaporation [1b], laser evaporation [3], thermal evaporation of carbon [1a], secondary ion mass spectrometry [4], and electron impact-induced elimination of C1 atoms from perchlorinated polycyclic aromatic hydrocarbons (PAHs) [5] were used. A noticeable development was the design and application of a

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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pulsed laser vaporization/supersonic expansion source [6] capable of generating intense carbon cluster beams having up to several hundreds of atoms in a cluster [7]. With the combination of this method and an ion mobility technique, called *ion chromatography* [8], the structures and the distribution of isomers of carbon cluster ions ranging from C_5 to C_{80} [9] have been successfully studied by von Helden et al. [1d] and Kemper et al. [8a] and Jarrold et al. [10]. The results demonstrated that the growth pattern of carbon cluster ions includes linear, monocyclic rings, polycyclic rings, and fullerenes. Linear structures exist up to $C_{10}^{\cdot+}$, and planar rings, bicyclic rings, and polycyclic rings are first observed at $C_7^{\cdot+}$, $C_{21}^{\cdot+}$, and $C_{30}^{\cdot+}$, respectively, and persist beyond $C_{40}^{\cdot+}$. Fullerenes appear first at $C_{30}^{\cdot+}$ and become the dominant species above $C_{50}^{\cdot+}$. Studies of the reactivity [1d,5] of pure carbon cluster ions are of interest, especially with respect to the structure–reactivity relationship within the series of carbon clusters and formation of isomeric species [11] for the different cluster sizes.

There are no reports of bulk isolation of pure carbon clusters of a size below C_{60} because of the very high chemical reactivity resulting from either unused “free dangling bonds” or strain energy in order to minimize the number of dangling bonds. However, it has been shown that it is possible to stabilize carbon cluster ions and to employ some of the unstable dangling bonds in covalent C–H bonding by adding hydrogen gas to the plasma forming the carbon clusters [12]. Studies of the structures of the resulting partially hydrogenated carbon clusters $C_nH_x^+$ ($n \leq 22$, $x \leq 5$) have been reported by Bowers et al. [12a,b] recently. It was found that addition of one, two, or a few more H atoms extended the range of linear species to $n = 15$ and $n \leq 22$, respectively, with a certain amount of monocyclic rings as the major isomer. Beyond $n = 15$ a new isomer appeared for $x \geq 4$ and persisted to $n \geq 22$. This isomer has been assigned to a bicyclic carbon cluster ion with a benzene ring and a carbon loop attached at its *ortho* positions. The appearance of such a species may indicate the starting point for the formation of PAHs in the carbon/hydrogen plasma. It has been proven that PAHs were formed in the plasma by adding a large amount of H_2 to the buffer gas [12e].

A different route to the formation of carbon cluster ions $C_n^{\cdot+}$ or partially hydrogenated carbon clusters $C_nH_x^+$ is the elimination of hydrogen ($H^{\cdot}$or H_2) from the molecular ions of PAHs. The loss of a hydrogen molecule H_2 (or $H^{\cdot}$) occurs on collision-induced dissociations (CIDs) [13] or surface-induced dissociations [14], and even as unimolecular dissociation of metastable ions [15]. However, most of the CID processes resulted in predominant fragmentation by loss of CH_x and/or C_2H_x as neutral fragments, especially at high collisional energies. In a recent study, Wang et al. [13c] have shown that losses of up to $4H^{\cdot}$(or $2H_2$) are the major processes by low energy collisions in an ion-trap mass spectrometer. In a related study by Nourse et al. [16], the stepwise elimination of H_2 from $C_{32}H_{19}^+$ ions was also reported, if these ions are generated by self ion–molecule reaction of pyrene ($C_{16}H_{10}$) in an ion-trap mass spectrometer.

The loss of hydrogen from ionized PAHs can only compete with other fragmentations if the C–H bond dissociation energy is small enough. The C–H bond energies and the critical energies of the bond cleavage activation of some PAH radical cations have been determined by Lifshitz et al. [17] by photoionization mass spectrometry. It was reported that the C–H bond dissociation energies of the radical cations of PAHs are about 3.61–4.67 eV. The critical energy of the bond cleavage of the benzene radical cation (3.61 or 3.88 eV) [18] is much lower than that of neutral benzene (4.7 eV) [19], owing to a C–H bond weakening effect in the ionized species. This is also observed for naphthalene [20], but apparently becomes negligible for larger PAHs such as anthracene and pyrene [21]. There are no reports about the C–H bond energy and the critical energy of the C–H bond cleavage of ions $C_nH_x^+$ arising from the loss of two or more hydrogen atoms from PAHs radical cations.

It is assumed that neutral and/or ionized C_nH_x clusters play an important role in the ion chemistry of interstellar clouds [22] and in combustion chemistry [23]. Ion–molecule reactions of carbon cluster ions have been proved to be a valuable method to distinguish isomeric species by evaluating the structure–reactivity relationship. For a rigorous study of cluster ions $C_nH_x^+$ by ion–molecule reactions, the controlled formation of $C_nH_x^+$ ions is mandatory. In this paper we report the preliminary results of an approach to prepare partially hydrogenated carbon clusters $C_nH_x^+$ and ionized carbon clusters $C_n^{\cdot+}$ in the gas phase by controlled stepwise eliminations of single hydrogen atoms from ionized PAHs. This method uses sustained off-resonance irradiation (SORI) [24] kinetically to excite the PAH ions by CID on a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer in a sequential mode (sequential SORI-CID). Because the procedure starts from the molecular ions of PAHs, this approach is complementary to studies generating the species $C_nH_x^+$ by laser vaporization of graphite in the presence of hydrogen, and it is of interest to compare the results of these two techniques to get more insight into the properties of these species.

2. Experimental

All PAHs used here were commercially available and were used without further purification (purity >99.5%).

The mass spectrometric experiments were performed using a Bruker CMS 47X FT-ICR mass spectrometer equipped with a 4.7 T superconducting magnet, an external electron ionization ion source [25], and an Infinity Cell [26]. The electron energy was set to 25–30 eV, and a filament current of 3.5–4.2 A was used. The temperature of the external ion source was 423–453 K. PAHs were introduced into the source by a temperature-controlled sample probe, and the temperature of the probe tip was adjusted to ~303–373 K, depending on the samples. The ions generated in the external source were transferred into the ICR cell where they were trapped at 298 K for the SORI experiment by applying trapping voltages of 0.9–1.5 V to the endcaps.

Before starting an SORI-CID experiment all unwanted ions were ejected by a standard procedure applying a combination of a chirp excitation (the peak-to-peak voltage, $V_{\text{p-p}}$, was ~45 V) and a series of radiofrequency pulses (“single shot”) at the natural cyclotron frequencies of the unwanted ions with mass-to-charge values close to the selected ion. The ion was then subjected to SORI-CID. Right before starting to accelerate the selected ions by SORI, a pulse of argon was admitted to the cell as the target gas for collisional activation. The peak pressures at the beginning of the SORI pulse were estimated to be $\sim 10^{-5}$ mbar. In order to observe only or at least predominantly the lowest dissociation pathway, ion activation by SORI [24] was achieved by setting an “off-resonance” irradiation pulse, where the frequency was set at 150–380 Hz aside from the natural cyclotron frequency of the selected ion. The duration of the pulse was adjusted to fit Eq. (1) where T_{SORI} (in seconds) is the duration of the SORI activation pulse, n is an integer between 2–6, which also stands for the number of acceleration/deceleration cycles, f_0 (in Herz) is the natural cyclotron frequency of the selected ion, and f^* (in Herz) is the irradiation frequency, which was always set lower (the corresponding mass-to-charge value is at the side higher in mass) than that of the selected ion in our experiments to avoid possible excitation of product ions.

$$T_{\text{SORI}} = n/|f_0 - f^*|[\text{s}] \tag{1}$$

Using this procedure, ions could be irradiated for long periods and made to collide many times with the atoms of the target gas without being lost from the cell. One of the major advantages of SORI-CID is that the dissociation products are formed close to the center of the ICR cell enabling a very efficient trapping for further tandem-mass spectrometry experiments. The average collision energy was carefully controlled by varying either the irradiation amplitude ($V_{\text{p-p}}$ about 0.5–0.9 V) or the frequency difference $\Delta f = f_0 - f^*$. To avoid any unintended excitation of the selected ions, the duration T_{ej} of the single shot ejection was set also according to the SORI theory [Eq. (1)]. After fragmentation by SORI-CID, all ions were detected with a standard excitation chirp to record the mass spectrum. Generally, the time span from generating the ions in the external ion source to their detection was about 0.5–1.5 s, depending on the number of steps of SORI used for dissociation.

Before inducing fragmentation by a next step of sequential SORI-CID, the product ion $C_nH_{x-1}^{+}$ from the previous step was selected as the "new" parent ion, and the other ions were ejected by the same procedure mentioned above. Then, SORI-CID was applied to realize the next low energy dissociation by slightly adjusting the parameters. For each PAH studied these fragmentation steps by SORI-CID were repeated until either the absolute intensity of the $C_nH_x^{+}$ ions was too low for further valid measurements because of the loss of ions from the cell or the pure carbon cluster ion $C_n^{\cdot+}$ was generated.

3. Results and discussion

Beginning each series of the sequential SORI experiment with the selected molecular ions of coronene ($C_{24}H_{12}^{\cdot+}$, m/z 300), perylene ($C_{20}H_{12}^{\cdot+}$, m/z 252), benz[a]anthracene ($C_{18}H_{12}^{\cdot+}$, m/z 228), chrysene ($C_{18}H_{12}^{\cdot+}$, m/z 228), triphenylene ($C_{18}H_{12}^{\cdot+}$, m/z 288), pyrene ($C_{16}H_{10}^{\cdot+}$, m/z 202), phenanthrene ($C_{14}H_{10}^{\cdot+}$, m/z 178), and fluorene ($C_{13}H_{10}^{\cdot+}$, m/z 166), respectively, an abundant product ion $[M\text{-}H]^{+}$ was observed in most cases by adjusting slightly the excitation energy and the frequency difference for SORI. The second elimination of a single hydrogen to produce the product ion $[M\text{-}2H]^{\cdot+}$ was achieved by choosing the ion $[M\text{-}H]^{+}$ from the first step as the parent ion for SORI activation. Continuing this procedure the hydrogen elimination reactions were followed in a stepwise manner as far as possible. A typical series of mass spectra is given in Fig. 1 for pyrene.

Usually the loss of $H^{\cdot}$ gives rise to the most abundant product ion of CID by SORI for the parent ions $C_nH_x^{+}$ of quite low hydrogen content. However, near the end of the series ($x \leq 6$) the combined losses of several hydrogen atoms and other fragmentations start to compete effectively. In the case of coronene ($C_{24}H_{12}^{\cdot+}$, m/z 300), at least seven steps of consecutive single hydrogen atom elimination reactions (reaction 1) were observed without any additional dissociation by losses of hydrocarbon fragments.

$$C_{24}H_{(+/12-x)} \rightarrow C_{24}H_{12-x-1}^{+} + H^{\cdot}(x = 0,\ 1\text{–}6) \quad (1)$$

As shown in Scheme 1, small amounts of multiple hydrogen elimination were observed for the SORI-CIDs of $C_{24}H_{12}^{\cdot+}$, $C_{24}H_{10}^{\cdot+}$, and $C_{24}H_{6}^{\cdot+}$. At the end of the coronene series, 35% of the $C_{24}H_{3}^{+}$ cluster ions fragment directly to $C_{24}^{\cdot+}$ and the other 65% of the $C_{24}H_{3}^{+}$ ions decompose by loss of hydrocarbon fragments and carbon atoms. $C_{24}H_{3}^{+}$ and $C_{24}^{\cdot+}$ are also produced from $C_{24}H_{6}^{\cdot+}$ without formation of $C_{24}H_{4}^{\cdot+}$, $C_{24}H_{2}^{\cdot+}$, and $C_{24}H^{+}$ as intermediates.

This stepwise SORI-CID of coronene molecular ions eventually yielding $C_{24}^{\cdot+}$ may be compared to other techniques that have been used to prepare $C_{24}^{\cdot+}$ or $C_{24}H_x^{+}$ ions. Previous studies [5] have shown that abundant carbon cluster ions $C_n^{\cdot+}$ may be produced directly from perchlorinated PAHs by electron ionization. However, competing dissociations by loss of chlorocarbon fragments occur because of the high excess energy of the molecular ions necessary to induce the consecutive losses of all chloro substituents after only a single energizing step. This is especially true for perchlorinated PAH, containing >18 C atoms. Hence, abundant $C_{24}^{\cdot+}$ could be formed from perchlorocoronene only by using multiple collisional activation with the multiple excitation collisional activation (MECA) technique [27]. The photodissociation of coronene radical ions within an FT-ICR cell resulted in consecutive losses of two hydrogen atoms (or probably loss of H_2) from $C_{24}H_{12}^{\cdot+}$ [28]. In this case, the total energy deposited on the ion was ~6–7 eV. By contrast, the SORI excitation energy used here certainly is lower. Therefore, mainly the dissociation process of the lowest energy is observed. The predominant H_2 elimination process was not observed until the collision energy was increased either by applying a stronger excitation field or by using a large number of acceleration/deceleration cycles. However, unintentional activation and/or ejection of product ions was observed during this high energy activation mode of SORI-CID, and this mode was not used routinely in this study.

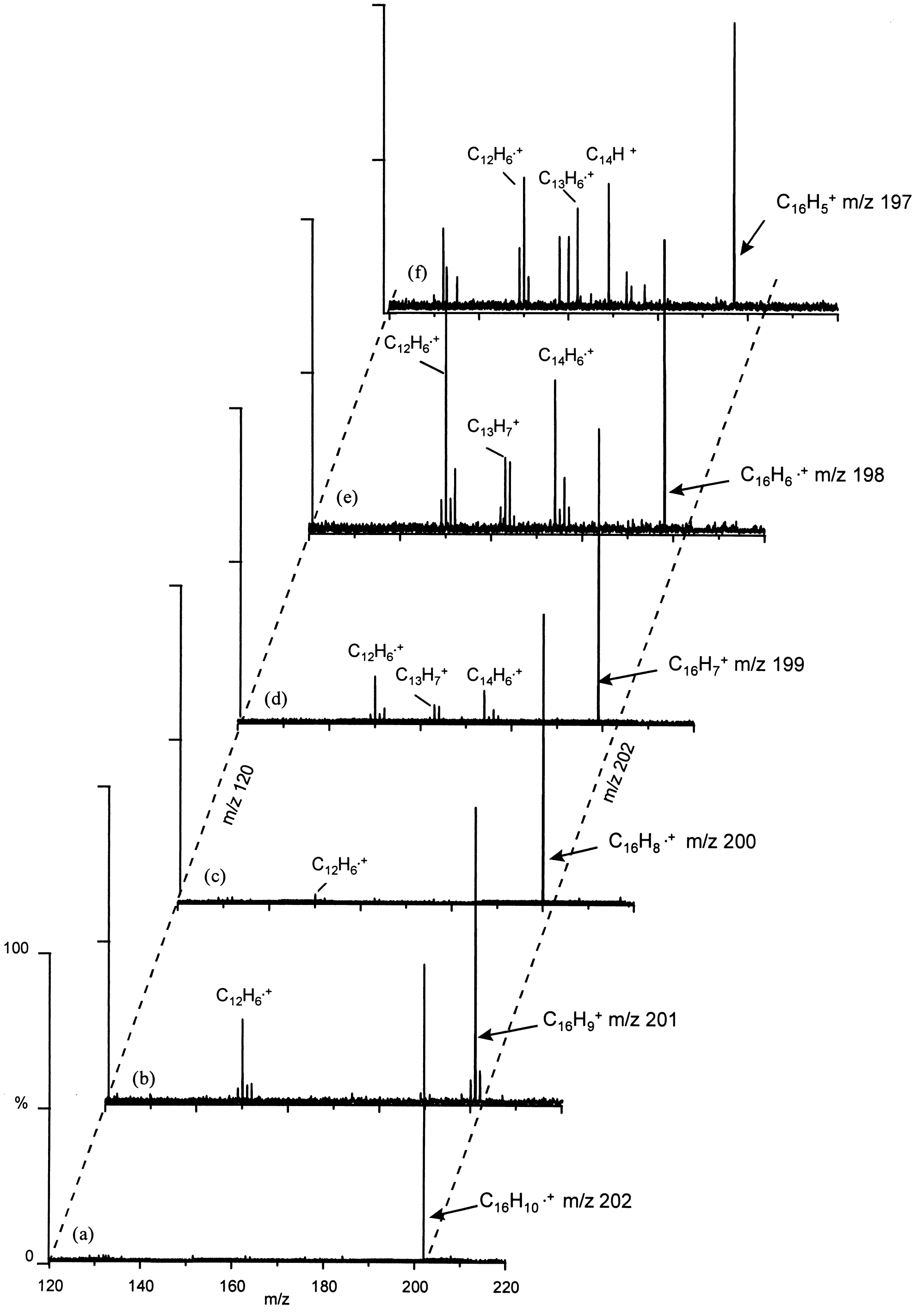
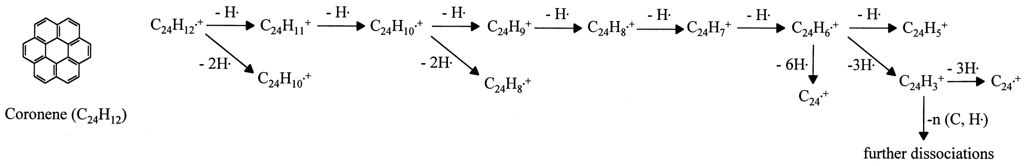
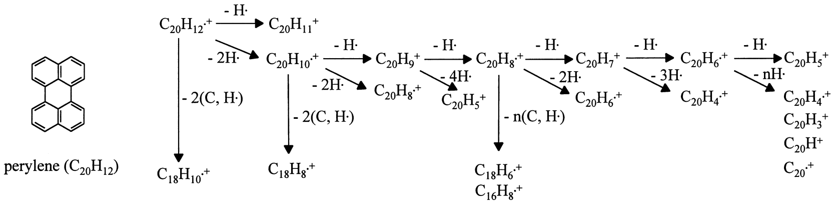


Fig. 1. Mass spectra of the stepwise hydrogen atom eliminations of the cluster cations $C_{16}H_x^+$ from pyrene by sequential SORI activation. (a) the isolated molecular ion of pyrene $C_{16}H_{10}^{\cdot+}$, *m/z* 202; (b) first step: formation of $C_{16}H_9^+$, *m/z* 201; (c) second step: formation of $C_{16}H_8^{\cdot+}$, *m/z* 200; (d) third step: formation of $C_{16}H_7^+$, *m/z* 199; (e) fourth step: formation of $C_{16}H_6^{\cdot+}$, *m/z* 198; and (f) fifth step: formation of $C_{16}H_5^+$, *m/z* 197.

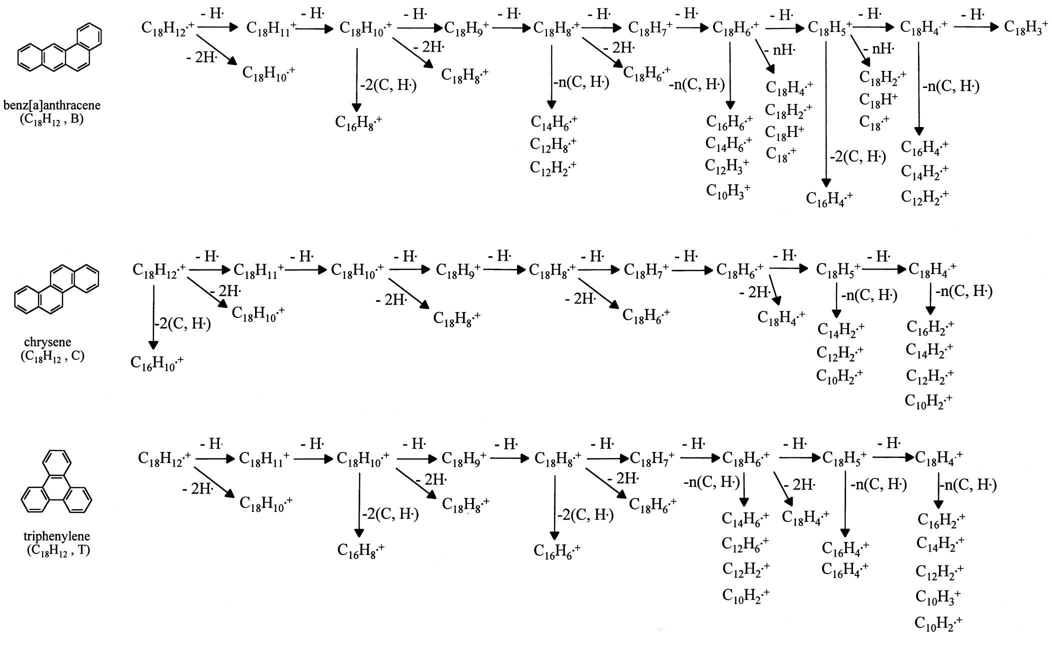


Scheme 1.

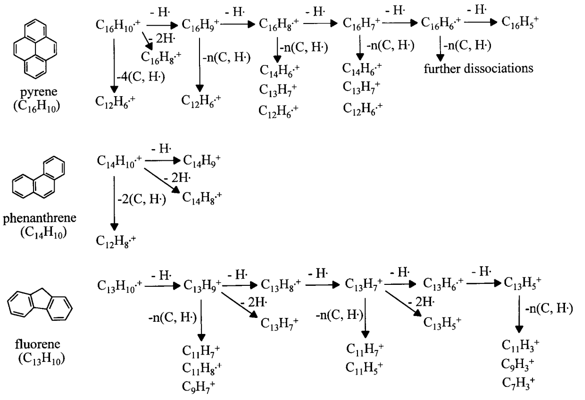
Schemes 2–4 summarize the dissociation channels of the other eight PAHs studied. Single hydrogen atom elimination was observed as the lowest dissociation pathway under the experimental conditions described above from the molecular ions of perylene ($C_{20}H_{12}^{\cdot+}$) (Scheme 2), benz[a]anthracene ($C_{18}H_{12}^{\cdot+}$), chrysene ($C_{18}H_{12}^{\cdot+}$), triphenylene ($C_{18}H_{12}^{\cdot+}$) (Scheme 3), pyrene ($C_{16}H_{10}^{\cdot+}$), phenanthrene ($C_{14}H_{10}^{\cdot+}$), and fluorene ($C_{13}H_{10}^{\cdot+}$) (Scheme 4). Besides hydrogen atom loss, further dissociation reactions occurred mainly for the radical cations $C_nH_{2m}^{\cdot+}$, e.g. $C_{24}H_{12}^{\cdot+}$, $C_{24}H_{10}^{\cdot+}$, and $C_{24}H_6^{\cdot+}$ from coronene (Scheme 1); $C_{20}H_{12}^{\cdot+}$, $C_{20}H_{10}^{\cdot+}$, $C_{20}H_8^{\cdot+}$, and $C_{20}H_6^{\cdot+}$ from perylene (Scheme 2); $C_{18}H_{12}^{\cdot+}$, $C_{18}H_{10}^{\cdot+}$, $C_{18}H_8^{\cdot+}$,



Scheme 2.



Scheme 3.



Scheme 4.

$C_{18}H_6^{\cdot+}$, and $C_{18}H_4^{\cdot+}$ from benz[a]anthracene, chrysene, and triphenylene (Scheme 3); $C_{16}H_{10}^{\cdot+}$, $C_{16}H_8^{\cdot+}$, and $C_{16}H_6^{\cdot+}$ from pyrene (Scheme 4); and $C_{14}H_{10}^{\cdot+}$ from phenanthrene (Scheme 4). Principally, product ions $C_nH_{2m}^{\cdot+}$ generated by loss of two *ortho* hydrogen atoms from PAH molecular ions are expected to be more stable [13c] because of the formation of acetylenic aryne bonds [16]. Consequently, an even electron species $C_nH_{2m+1}^{+}$ is expected to dissociate more easily by loss of a single hydrogen atom to form a more stable product ion $C_nH_{2m}^{\cdot+}$. Indeed, for the SORI-CID technique used in this study, loss of a single hydrogen atom from cluster ions $C_nH_{2m+1}^{+}$ occurred even in the regime of very low excitation energy. Naturally, the product ions $C_nH_{2m}^{\cdot+}$ have a different frequency from that of the parent ion $C_nH_{2m-1}^{+}$ and the further irradiation did not affect them at all. As a result, very few other fragmentations besides loss of $H^{\cdot}$ were observed for this kind of ion. Conversely, the more stable odd electron species $C_nH_{2m}^{\cdot+}$ had to accumulate more energy by multiple collisions with argon gas in the cell. Therefore, they also suffered some other high energy fragmentations by loss of hydrocarbon fragments besides loss of a single hydrogen atom. The molecular ion of phenanthrene $C_{14}H_{10}^{\cdot+}$ and fluorene $C_{13}H_{10}^{\cdot+}$ (Scheme 4) behave exceptionally. From the former ions only two consecutive hydrogen eliminations were observed because the molecular ions fragmented to almost 70% by loss of C_2H_2. This is known to be a low energy process also occurring in metastable molecular ions [13a]. Further hydrogen elimination was unsuccessful because of the lack of the ion intensity. In the case of ionized fluorene only the cluster ions $C_{13}H_9^{+}$, $C_{13}H_7^{+}$, and $C_{13}H_5^{+}$ with the even electrons exhibited additional fragmentations. Fluorene contains an odd number of carbon atoms and a nonaromatic CH_2 group. Therefore, a very stable ion is formed by loss of one hydrogen atom. This stability is retained for the other cluster ions $C_{13}H_{2m+1}^{+}$. Thus, the behavior of ionized fluorene is still consistent with the behavior of the radical cations $C_nH_{2m}^{\cdot+}$ mentioned above.

Another even more interesting feature is the range of the hydrogen eliminations that can be observed in series by sequential SORI-CID for the individual PAH ions as illustrated in Table 1. In most cases, the sequence of predominant single hydrogen elimination is confined to the formation of $C_nH_5^{+}$, which derives from $C_{24}H_{12}^{\cdot+}$ and $C_{20}H_{12}^{\cdot+}$ by seven steps of single hydrogen atom elimination, and from $C_{16}H_{10}^{\cdot+}$ and $C_{13}H_{10}^{\cdot+}$ by five steps, at least under our experimental conditions. For $C_nH_5^{+}$, no further abundant single hydrogen elimination was observed with the exception of these ions derived from $C_{18}H_{12}^{\cdot+}$ (benz[a]anthracene, chrysene, triphenylene) either because of competing dissociation by loss of carbon or hydrocarbon fragments or because of insufficient ion intensity, even though the formation of $C_nH_x^{+}$ with $x < 5$ is detected under identical conditions as minor processes from $C_nH_x^{+}$ with $x \geq 6$. This is very consistent with the study of the structures and the formation of $C_nH_x^{+}$, $x < 5$, by Lee et al. [12a] and Bowers [12b], using a laser vaporization/supersonic expansion source. These authors found that, by adding hydrogen to carbon cluster ions $C_n^{\cdot+}$ ($9 \leq n \leq 22$), the structures of the species generated changed from monocyclic $C_n^{\cdot+}$ to linear structures of $C_nH_x^{+}$ ($x \leq 3$). Furthermore, a new bicyclic isomer appeared as a minor species from $x = 4$ ($n \geq 15$), which became more rapidly abundant with increasing n by suppressing both linear and monocyclic isomers in most cases. For the three cluster ions with $x = 5$ ($C_{18}H_5^{+}$, $C_{17}H_5^{+}$, and $C_{16}H_5^{+}$) produced in their study, the percentages of the bicyclic isomers increased significantly [12a]. Semiemperical PM3 calculation [29] of the most

Table 1
Products of consecutive hydrogen atom elimination and relative abundances starting from $PAH^{\cdot +}$ by sustained off-resonance irradiation activation

	Relative abundance of $C_nH_x^+$ resulting from hydrogen elimination										
						$x =$					
$PAH^{\cdot +j}$	11	10	9	8	7	6	5	4	3	2	1	0
$C_{24}H_{12}^{\cdot +}$	91[a]	100[a]	97	00[a]	100	100[a]	64	—	22[b]	—	—	35[c] (14[b])
$C_{20}H_{12}^{\cdot +}$	8	84[d]	63	100[a] (20[e])	63	91 (18[f])	48	15[g]	10[g]	—	18[g]	9[g]
$C_{18}H_{12}^{\cdot +}$ (B)	34	100	44	100	64	100	29	55	7	7[h]	19[h]	7[h]
$C_{18}H_{12}^{\cdot +}$ (C)	41	100	86	100	77	100	65	74	0	—	—	—
$C_{18}H_{12}^{\cdot +}$ (T)	66	100	33	100	60	100	46	84	0	—	—	—
$C_{16}H_{10}^{\cdot +}$			63	99[a]	81[a]	76 [a]	50[a]	—	—	—	—	—
$C_{14}H_{10}^{\cdot +}$			26	8[i]	—	—	—	—	—	—	—	—
$C_{13}H_{10}^{\cdot +}$			100[a]	70	100	85	100[a]	—	—	—	—	—

[a] The parent ion $C_nH_x^+$ has fragmented to $C_nH_{x-1}^+$ with 100%.
[b] From $C_{24}H_6^{\cdot +}$.
[c] From $C_{24}H_3^{\cdot +}$.
[d] From $C_{20}H_{12}^{\cdot +}$.
[e] From $C_{20}H_{10}^{\cdot +}$.
[f] From $C_{20}H_8^{\cdot +}$.
[g] From $C_{20}H_6^{\cdot +}$.
[h] From $C_{18}H_5^{\cdot +}$.
[i] From $C_{14}H_{10}^{\cdot +}$.
Key: $C_{18}H_{12}^{\cdot +}$ (B), $C_{18}H_{12}^{\cdot +}$ (C), and $C_{18}H_{12}^{\cdot +}$ (T), benz[a]anthracene, chrysene, and triphenylene, respectively.

stable structure of $C_{16}H_4^{\cdot +}$ isomers [12a] showed that bicyclic $C_{16}H_4^{\cdot +}$ are much more stable than linear (~126–377 kJ/mol higher in heat of formation) and monocyclic isomers (~711–962 kJ/mol higher), especially for the most stable structure containing an benzene ring *ortho* substituted by a carbon loop. Furthermore, it has been reported [30] previously that the cations $C_{12}C1_4^{\cdot +}$ retained the original PAH skeleton despite the loss of up to six C1 substituents from decachloroacenaphthene. In a separate study, which will be published elsewhere, we investigated the ion–molecule reactions of $C_nH_x^+$ ($n \geq 20$, $x \leq 10$) [31], and the results also indicate that the structure of the original PAH was obviously remembered to some degree by the ions $C_nH_x^+$ with $x \leq 4$. For ions $C_nH_x^+$ arising in the experiments discussed here by hydrogen eliminations induced by low energy ("soft") SORI, it is reasonable to assume that the PAH structures are kept or are modified only slightly by rearrangements into polycyclic structures. However, apparently a more dramatic structural change occurs during the transition from $C_nH_5^+$ to $C_nH_4^{\cdot +}$, which requires more energy for the loss of further H atoms because of the accompanying rearrangements into linear or monocyclic structures. Among the PAHs investigated here, abundant ions $C_nH_4^{\cdot +}$ are generated only from the molecular ions of benz[a]anthracene, chrysene, and triphenylene (Scheme 3) by the stepwise elimination of 8 H atoms. It is intriguing that all these PAHs already contain the structural element of an *ortho* substituted benzene moiety suggested as the most stable structure of $C_nH_4^{\cdot +}$, if a terminal benzene ring is retained and the other rings are converted into the C_n chain of the loop during the loss of hydrogen atoms. Regardless, the agreement between the previous studies [12a,b] and our experiments gives credit to the suggested bicyclic structure of $C_nH_4^{\cdot +}$.

However, experiments to create the pure carbon cluster cations $C_n^{\cdot +}$ from PAH molecular ions by SORI were unsuccessful in most cases. The difficulty to form $C_nH_x^+$ ($x \leq 4$) by the "soft" SORI activation may be an important reason for this. Additionally, the loss of the ion intensity during the SORI activation is still a problem. The efficiency of each SORI activation process is ~80–90%, and after six to eight steps of SORI activations, the ion intensity is only ~10–

20% of the original intensity of the isolated molecular ions, especially for the PAHs with <18 C atoms. For example, for the $C_{16}H_x^+$ cluster ions from pyrene shown in Fig. 1, the noise levels of the last two steps of SORI activations are so high it is impossible to observe the hydrogen atom elimination during the further step. In addition, at these low ion intensities some other ions escaping the ejection procedures of the previous SORI steps or even small amounts of ions invading from the external source during the long trapping periods, such as $C_{12}H_8^{\cdot+}$, $C_{13}H_8^{\cdot+}$, and $C_{14}H_8^{\cdot+}$ in Fig. 1(e) and $C_{12}H_7^+$ and $C_{13}H_7^+$ in Fig. 1(f), start to appear in the mass spectra and terminate meaningful SORI experiments.

As mentioned before, Lifshitz et al. [17] have shown that the C–H bond energies of the molecular ions of pyrene ($C_{16}H_{10}^{\cdot+}$) and triphenylene ($C_{18}H_{12}^{\cdot+}$) are 4.60 eV and 3.73 eV, respectively, which are needed at least for the elimination of the first hydrogen atom. There are no reports available of the critical energy for a stepwise elimination of more than one hydrogen atom or of the C–H bond energy in $[M\text{-}H]^+$ fragment ions of PAHs. It is difficult to measure directly the excess energy deposited on the ions by the SORI activation. An investigation using SORI activation to determine the dissociation energy of the C–H bonds of the ions $C_nH_{2m+1}^+$ and $C_nH_{2m}^{\cdot+}$ from this work is in progress.

4. Conclusions

The dissociation processes of lowest activation energy for ionized PAHs usually correspond to a stepwise elimination of single hydrogen atoms. This process has been investigated by the SORI technique of FT-ICR mass spectrometry for nine selected polycyclic aromatic hydrocarbons containing between 13 and 24 C atoms. As expected, the loss of a single hydrogen atom from the molecular ions of the PAHs is the most intense fragmentation. Performing sequential SORI-CID by selecting the fragment ions $[M\text{-}H]^+$ in the FT-ICR cell for the next SORI experiment, the sequential losses of single hydrogen atoms can be followed over several steps until hydrogenated carbon cluster ions $C_nH_x^+$ with a rather low hydrogen content are formed. For most of the cluster ions $C_nH_x^+$, the observed fragmentations are also dominated by the elimination of a single hydrogen atom to form $C_nH_{x-1}^{\cdot+}$, especially for $x = 2m + 1$. Ions $C_nH_x^{\cdot+}$ with $x = 2m$ exhibit significant additional dissociations by loss of hydrocarbon fragments or by multiple hydrogen eliminations. A related odd/even regularity is also observed in the case of the odd number of carbon PAH, fluorene. The common feature of the collision-induced decomposition of the ionized PAHs by sequential SORI-CID is to form eventually $C_nH_5^+$ after five or seven steps of single hydrogen elimination. Additional hydrogen elimination to produce $C_nH_4^{\cdot+}$ or pure carbon cluster ion $C_n^{\cdot+}$ was shown to be more difficult and was successful only with certain ionized PAHs. The resistance to form $C_nH_4^{\cdot+}$ by further loss of H can be attributed to a structural rearrangement during the formation of $C_nH_4^{\cdot+}$. This would corroborate the specific stable structure of $C_nH_4^{\cdot+}$ ions corresponding to a benzene moiety that is *ortho* substituted by a loop of C atoms. In line with this argument, $C_nH_4^{\cdot+}$ ions are formed more easily by SORI-induced loss of 8 H atoms from the molecular ions of benz[a]anthracene, chrysene, and triphenylene, which already contain the structural element of the stable ions $C_nH_4^{\cdot+}$. Although it was not possible to produce abundant carbon cluster ions $C_n^{\cdot+}$ with a preselected carbon atom number n from the readily available PAHs, the SORI-CID technique proved to be a convenient method to generate hydrogenated carbon cluster ions $C_nH_x^+$ of rather low hydrogen content. It is suspected that these hydrogenated carbon cluster compounds are important intermediates for the formation of PAH and probably also of fullerenes in hydrocarbon flames, and their ion–molecule reactions are under study now by FT-ICR mass spectrometry.

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