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General trends in dissociations of medium-sized hydrocarbon dications

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Dedicated to Professor Eugen Illenberger on the occasion of his 65th birthday.

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ABSTRACT

This study aims towards a rationalization and generalization of the fragmentation patterns of medium-sized hydrocarbon dications by tandem mass spectrometry. Phenanthrene ($C_{14}H_{10}$) serves as a precursor for the generation of $C_mH_n^{2+}$ dications with $m = 9$–14 and $n = 1$–10. Four characteristic channels occur in the metastable-ion spectra: loss of a hydrogen atom, elimination of molecular hydrogen, loss of acetylene, and charge-separation fragmentation (Coulomb explosion). The first two channels dominate the spectra and their relative intensities show some regularities for ions with an even number of carbon atoms. Further, parent ions with an odd number of hydrogen atoms exhibit loss of atomic hydrogen, whereas loss of molecular hydrogen is preferred for dications with an even number of hydrogen atoms. The ions with odd number of carbon atoms do not show any evident regularity for the H and H_2 losses. The channels involving C—C bond cleavages occur for larger dications with $m > 9$, but only for some combinations of m and n without an apparent regularity.

1. Introduction

Interstellar clouds, nebulas, and upper atmospheres of gas giants are expected to contain many organic compounds including polycyclic aromatic hydrocarbons (PAHs) [1–3]. The mechanism of the formation of PAHs in these environments is not precisely known and many possible scenarios have been proposed [4–7]. Recently, it has been suggested that PAHs might be present in the interstellar medium also in their doubly ionized state [8] and these dications might be even responsible for the extended red emission [9]. Interestingly, dications also provide a feasible and efficient route for the growth of PAHs in environments with extremely low temperatures and pressures. We have shown that medium-sized dications $C_mH_n^{2+}$ react with molecules such as methane (Eq. (1)) [10], acetylene (Eq. (2)) [11], or benzene (Eq. (3)) [12] to yield larger dications. The formation of the final doubly charged product is enabled by the occurrence of the loss of atomic or molecular hydrogen from the doubly charged intermediate (adduct); the dehydrogenation reactions serve as a "cooling" process and prevent the dissociation of the doubly charged intermediates to two singly charged fragments in the course of the coupling reaction [13].

$$C_nH_m{}^{2+} + CH_4 \rightarrow [C_{n+1}H_{m+4}]^{2+} \rightarrow C_{n+1}H_{m+2}{}^{2+} + H_2 \quad (1)$$

$$C_nH_m{}^{2+} + C_2H_2 \rightarrow [C_{n+2}H_{m+2}]^{2+} \rightarrow C_{n+2}H_m{}^{2+} + H_2 \text{ or } C_{n+2}H_{m+1}{}^{2+} + H \quad (2)$$

$$C_nH_m{}^{2+} + C_6H_6 \rightarrow [C_{n+6}H_{m+6}]^{2+} \rightarrow C_{n+6}H_{m+4}{}^{2+} + H_2 \quad (3)$$

The abundant losses of atomic and molecular hydrogen from hydrocarbon dications, which largely exceed related dehydrogenation processes of neutral or singly charged hydrocarbons, can be rationalized in two ways. One may argue that dications are usually generated under rather energetic conditions and thus contain considerable amount of excess internal energy, which accordingly leads to increased fragmentations as compared to neutral or singly charged molecules. Alternatively, the energy demands for the H and H_2 eliminations may be significantly smaller for the doubly charged ions than for the corresponding singly charged ions, and the pronounced tendency for excessive dehydrogenation would thus correspond to an intrinsic property of hydrocarbon dications.

Considering the second explanation presented above, let us refer to the known energetics for the hydrogen eliminations from neutral, singly, and doubly charged benzene (Scheme 1) [14–20]. Elimination of a hydrogen atom from neutral benzene requires almost 5 eV. This value drops to 4 eV for singly charged benzene, and the H elimination from the benzene dication requires only 3.3 eV. The decreasing amounts of energy required for the H atom eliminations are accordingly associated with lower ionization energies of hydrogen-depleted C_6-hydrocarbons. This, of course, is not a strict

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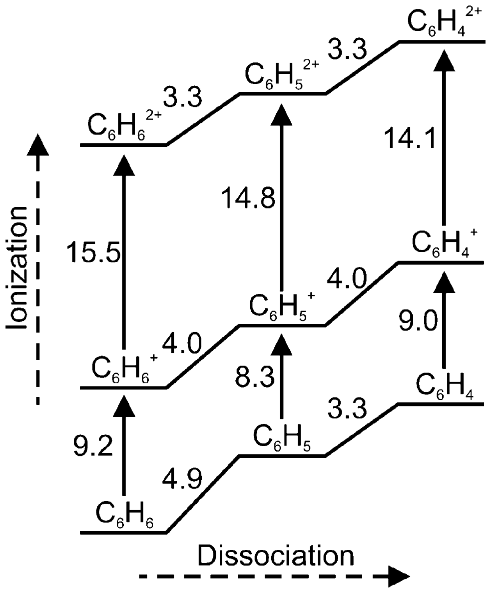

Scheme 1. Schematic energy diagram of the sequential cleavage of C—H bonds in benzene. All the energies are given in eV.

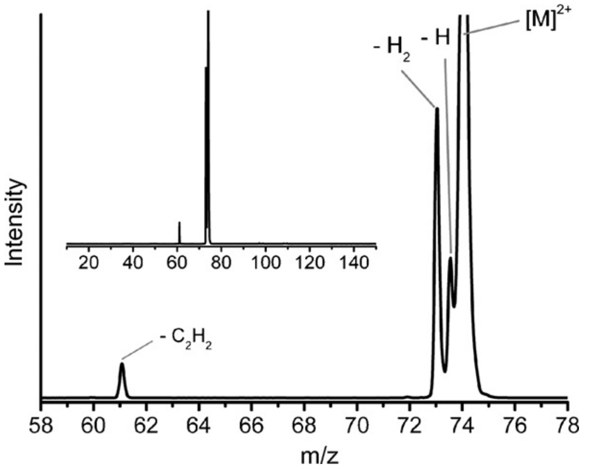

Fig. 1. MI spectrum of the mass-selected dication with $m/z = 74$. The inset shows the MI spectrum with whole scan range of mass (parent ion is off-scale).

rule as demonstrated by the increase of the ionization energy from C_6H_5 to C_6H_4, but it provides a plausible reasoning for the greater facility for dehydrogenation of hydrocarbon dications with respect to their neutral and singly charged counterparts.

In the following, we aim at unraveling general trends in H and H_2 eliminations from medium-sized hydrocarbon dications and use this information to predict the pattern of products from bond-forming reactions of hydrocarbon dications.

2. Experimental

The experiments were made on a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric field) described elsewhere [21]. Briefly, the desired ions were generated by electron ionization of neutral phenanthrene, accelerated by an electric field of 8 kV, and mass-selected by means of B(1)/E(1). The unimolecular fragmentations of metastable ions (MIs) occurring in the field-free region preceding the second magnet were monitored by scanning B(2). All spectra were accumulated with the AMD-Intectra data system; 5–10 scans were averaged to improve the signal-to-noise ratio. All data were corrected for contributions of ^{13}C isotopes [22,23] and intensities were normalized to 1000. In addition to fragmentation patterns, the relative fractions of dissociation X are evaluated from all spectra according to Eq. (4), where I_f means intensity of fragments in a spectrum, I_P means intensity of the parent ion, and N is number of fragment peaks in a spectrum. Further, the multiplier voltage was adjusted so that intensity of the parent ion did not exceed 80% of the detector's limit and the linear response of the multiplier for the parent ion as well as for the fragments was checked by the variation of the multiplier voltage.

$$X = \frac{\sum_{f=1}^{N} I_f}{I_P + \sum_{f=1}^{N} I_f} \qquad (4)$$

The theoretical studies employed the density functional method B3LYP [24,25] in conjunction with TZVP basis sets as implemented in the Gaussian 03 package [26]. Harmonic vibrational frequencies and zero point vibrational energies (ZPVEs) were computed at the same level of theory from analytically derived Hessian matrices by standard routines implemented in the Gaussian program. Many possible isomers for the studied dications $C_3H_n{}^{2+}$ and $C_4H_n{}^{2+}$ were localized and the results reported below refer to the most stable ones found. The full account of the calculations together with the optimized geometric structures of the dications can be found in the Supplementary Material.

3. Results and discussion

Phenanthrene was chosen as a precursor molecule for the generation of $C_mH_n{}^{2+}$ dications with a mass range from $m/z = 55$ to $m/z = 89$. It is assumed that under the conditions of the ion generation, complete randomization of the structure of the ions is achieved and therefore the structure of the precursor molecule itself does not significantly influence the chemical behavior of the ions generated [23]. This assumption is based on the experimental finding, which shows that the electron-ionization source provides not only enough energy for double ionization, but also the internal energies of the formed dications are high enough such that the isomerization barriers can be surmounted easily [23]. Although it may not be fully justified in all cases, the assumption of a fair amount of equilibration to the energetically lowest lying structures is reasonable and presumably sufficient as a first-order approximation for the present screening purposes about the general behavior of $C_mH_n{}^{2+}$ dications.

The dominant channels in the unimolecular fragmentations of metastable dications $C_mH_n{}^{2+}$ correspond to losses of atomic and molecular hydrogen accompanied by a loss of acetylene and charge-separation reactions. The relative abundances of these channels depend on the number of carbon and hydrogen atoms in the $C_mH_n{}^{2+}$ dications.

Fig. 1 shows the MI spectrum of $C_{12}H_4{}^{2+}$ as an illustration, where the losses of a hydrogen atom ($m/z = 73.5$), molecular hydrogen ($m/z = 73$), and acetylene ($m/z = 61$) can be clearly detected. The two first processes can be found for all dications studied. Elimination of acetylene is observed for larger dications, roughly with more than 10 carbon atoms. The next illustrative spectrum shows the fragmentation of $C_{10}H_6{}^{2+}$ with mass-to-charge ratio $m/z = 63$ (Fig. 2). Besides the losses of atomic and molecular hydrogen as well as acetylene, a double elimination of H_2 can be observed ($m/z = 61$), which is treated together with a single H_2 molecule ($m/z = 62$) in the following analysis. Finally, for this precursor dication also Coulomb explosion (CE) to $C_7H_3{}^+$ and $C_3H_3{}^+$ is evident in the spectrum (Eq. (5)). The corresponding peaks (see insets in Fig. 2) have

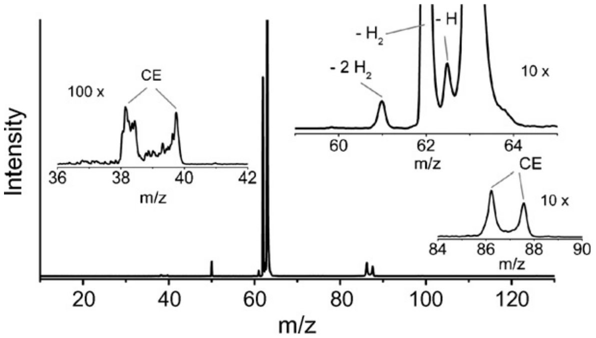

Fig. 2. Example of an MI spectrum of $C_{10}H_6{}^{2+}$ ($m/z = 63$). The insets show the losses of atomic and molecular hydrogen and two peaks due to Coulomb explosions according to Eq. (5).

typical dished-top shapes, which reflect a substantial kinetic energy release upon separation of the two positively charged fragments [27].

$$C_{10}H_6{}^{2+} \rightarrow C_7H_3{}^+ + C_3H_3{}^+ \qquad (5)$$

The data summarized in Table 1 shows the predominance of the eliminations of atomic and molecular hydrogen in the fragmentations of medium-sized PAHs dications. A plausible explanation stems most probably from the fact that the hydrogen rearrangements are usually associated with relatively low energy barriers [28–31] and dissociation limits for the favored H and H_2 eliminations are well below the Coulomb barriers for the charge-separation processes [32–34]. Thus, in the time window of the MI experiment, the dications can undergo a series of rearrangements towards a structure, for which the dehydrogenation is favored and subsequently eliminate H or H_2. Note that if the internal energy of generated dications is well above the barriers for Coulomb explosion, the direct separation can be preferred [35–37].

For ions with an even number of carbon atoms m, two general trends can be observed. Firstly, the relative fraction of dissociation (X) of $C_mH_n{}^{2+}$ shows an oscillating behavior with the number of hydrogen atoms n in that the fragmentation of dications with an odd number of hydrogen atoms is usually more pronounced. Secondly, the dications with an even number of hydrogen atoms usually preferentially eliminate molecular hydrogen [35–37], whereas the dications with an odd number of hydrogen atoms preferentially lose atomic hydrogen (Fig. 3). The regularity in the stabilities and fragmentation patterns can be most probably ascribed to the fact that dications with odd number of hydrogen atoms are open-shell species presumably with doublet ground state [23], whereas those with even number of hydrogen atoms are closed-shell species, most likely with singlet ground states [19,22,27,32]. The open-shell dications can therefore more easily lose a hydrogen radical, whereas the closed-shell dications preferentially eliminate an H_2 molecule. In some configurations, dications with even number of hydrogen atoms can have triplet ground state [32,38], which may be responsible for some exceptions from the general trends observed in the measurements (e.g., a relatively large X is observed for $C_{14}H_8{}^{2+}$ together with a prevailing loss of a hydrogen atom compared to H_2 loss).

Compared to the dications with an even number of carbon atoms, the dications with odd number of carbon atoms show a more pronounced population of Coulomb explosions (dications $C_9H_n{}^{2+}$) and more abundant acetylene eliminations (dications $C_{13}H_n{}^{2+}$). Both channels usually require a higher activation energy as compared to the H and H_2 losses. Accordingly, it can be assumed that the odd carbon dications are generated with relatively large internal energies and their fragmentations are therefore less specific.

Table 1
Relative abundances of major fragmentation of $C_mH_n{}^{2+}$ with $m = 9–14$[a]

m	n[b]	X [%][c]	x_H	x_{H_2}	$x_{C_2H_2}$	x_{CE}
9	2	1×10^{-2}	1000	<0.1	–	–
	3	2.79	1000	<0.1	–	–
	4	3.78	37	963	–	–
	5	1.29	–	908	–	92
	6	2.84	272	275	–	453
	7	1×10^{-2}	220	345	–	435
	8	1×10^{-2}	379	621	–	–
	9	1×10^{-2}	120	<0.1	–	880
	10	1×10^{-2}	–	699	–	301
10	1	1.05	1000	–	–	–
	2	1×10^{-2}	–	913	–	87
	3	1.79	1000	<0.1	–	–
	4	1×10^{-2}	158	842	–	–
	5	2.31	868	93	–	40
	6	1×10^{-2}	14	831	61	94
	7	1×10^{-2}	640	42	131	187
	8	1.69	–	942	58	–
	10	1×10^{-2}	–	1000	–	–
11	1	6.07	1000	–	–	–
	2	1×10^{-2}	815	185	–	–
	3	3.22	995	5	–	–
	4	1×10^{-2}	141	129	730	–
	5	1×10^{-2}	207	354	294	145
	6	1×10^{-2}	–	657	–	343
	7	1×10^{-2}	672	163	78	87
	8	9.75	456	544	–	–
	9	8.36	367	533	100	–
	10	1×10^{-2}	690	310	–	–
12	1	4.07	1000	–	–	–
	2	1×10^{-2}	449	48	–	502
	3	3.57	1000	<0.1	–	–
	4	1×10^{-2}	197	713	89	–
	5	3.62	817	28	155	–
	6	1×10^{-2}	–	641	311	48
	7	7.51	949	51	–	–
	8	1.33	97	113	790	–
	10	1×10^{-2}	63	229	709	–
13	1	4.23	1000	–	–	–
	2	1×10^{-2}	108	256	577	59
	3	1×10^{-2}	716	65	219	–
	4	2.13	114	75	811	–
	5	2.17	–	22	920	58
	6	1.08	–	97	834	70
	7	5.18	928	53	19	–
	8	4.95	756	192	52	–
	9	5.11	673	141	186	–
	10	6.95	249	706	45	–
14	1	7.42	1000	–	–	–
	2	1×10^{-2}	51	949	–	–
	3	5.37	1000	<0.1	–	–
	4	1×10^{-2}	–	983	17	–
	5	2.62	106	<0.1	864	30
	6	1×10^{-2}	–	803	197	–
	7	0.74	1000	<0.1	–	–
	8	3.33	473	47	479	–
	9	5.65	975	6	20	–
	10	2.60	16	198	786	–

[a] $x_f = I_f/\Sigma I_f$, where I_f is intensity of the fragment in the spectrum, and ΣI_f means sum of intensities of all fragments in the spectrum. A label H corresponds to the atomic hydrogen loss, H_2 to the loss of molecular hydrogen, C_2H_2 to the loss of acetylene, and CE to the sum of intensities of the products due to Coulomb explosion.

[b] Dications C_9H^{2+}, $C_{10}H_9{}^{2+}$, and $C_{12}H_9{}^{2+}$ were not generated in an amount permitting the experiment.

[c] X [%] is the relative fraction of dissociation as defined in Section 2.

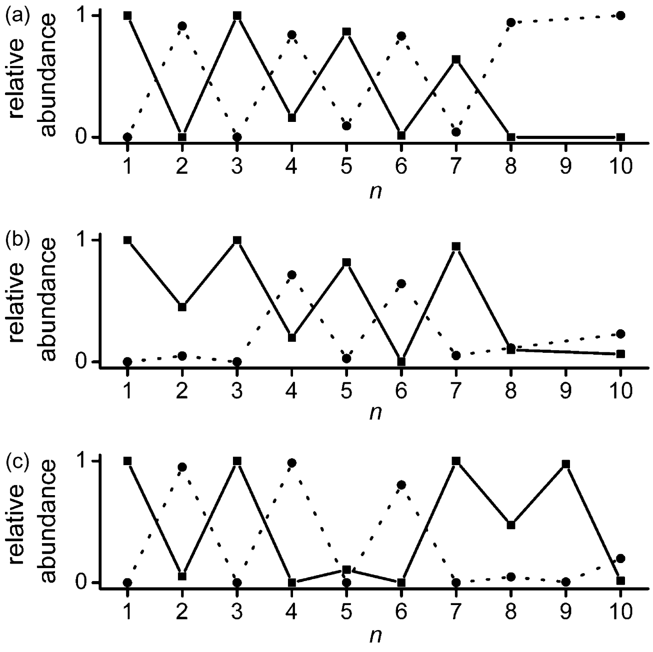

Fig. 3. Relative abundances of the hydrogen-atom loss (solid line with square symbols) and that of molecular hydrogen (dotted line with circle symbol) as a function of the number of hydrogen atoms n in the parent dications $C_mH_n^{2+}$, where m equals to (a) 10, (b) 12, and (c) 14, respectively.

This is most probably also the reason, why no regularities in fragmentations of these dications are observed. The fragmentations of the $C_{13}H_n^{2+}$ dications are particularly illustrative with large values of X for all n, excluding $n = 2$ and 3 and large abundances of acetylene eliminations. Note that all dications studied here are generated by electron ionization of phenanthrene and the fragmentation mechanism leading to a particular dication will influence its internal energy. In particular, losses of C-fragments with even number of carbon atoms from hydrocarbon dications are largely preferred [39], hence eliminations of odd-carbon atom fragments most probably require more energetic conditions.

As far as the loss of acetylene is concerned, this decomposition channel is usually preferred for larger dications. This finding can be rationalized easily, because for smaller dications the loss of neutral acetylene represents a more drastic size reduction of the skeleton, in which the two charges are localized. Specifically, the loss of acetylene occurs mainly for $m \geq 10$ and $n \geq 4$ in the parent ion $C_mH_n^{2+}$. For $m = 10$, this channel peaks with low relative abundance around $n = 7$. If $m = 11$, the elimination of C_2H_2 dominates for $n = 4$ and 5, with a small relative abundance it also contributes to fragmentation of $C_{11}H_n^{2+}$ with $n = 7$ and 9. For $m = 12$, the relative abundance of the C_2H_2 loss is rising from $n = 4$ to 6, for $n = 7$, it is not present and the reaction dominates for $n = 8$ and 10. For $m = 13$, loss of C_2H_2 is observed for all $n > 1$ and corresponds to the major channel for $n = 4$–6. In hydrocarbon dications with 14 carbon atoms, the C_2H_2 elimination dominates for $n = 5$ and 10 and it is one of two major processes for $n = 8$. Thus, the C_2H_2 loss plays a more important role for the hydrocarbon dications $C_mH_n^{2+}$ with higher values of m and n. A comparison between the relative abundances of C_2H_2 loss and the conversion fraction X leads to the conclusion that C—C cleavage processes require more energy than the H or H_2 losses, because larger fractions of the C_2H_2 elimination are coupled with large values of X. On the other hand, exceptions are observed for cases where probably an energetic preference for the formation of a more stable product favors the elimination of C_2H_2.

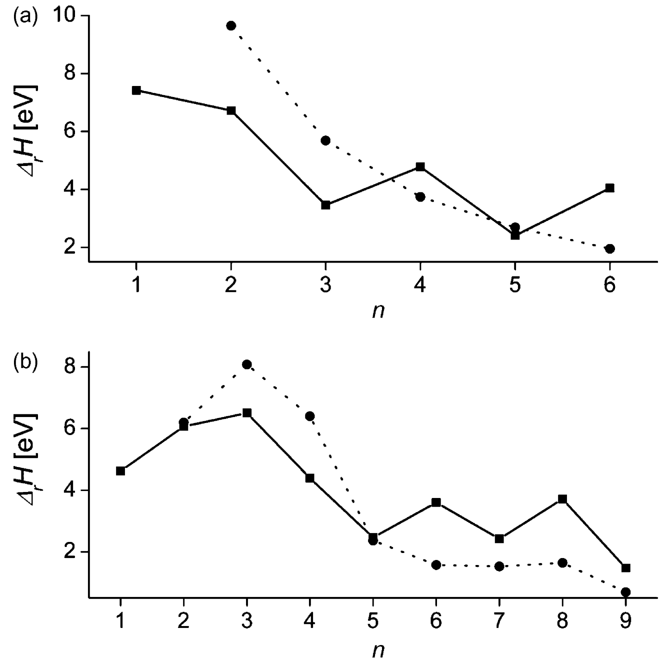

Fig. 4. Dissociation enthalpies $\Delta_r H$ of $C_3H_n^{2+}$ dications (a) and of $C_4H_n^{2+}$ dications (b). The solid line with square points is assigned to the loss of a hydrogen atom and the dotted line with circle points is assigned to the loss of molecular hydrogen.

Next, the charge-separation processes are addressed briefly. For medium-sized hydrocarbon dications, this path represents only a minor channel and it plays an important role only for $C_9H_n^{2+}$, where CEs occur as competing channels to the losses of molecular hydrogen. Coulomb explosion is also detected for $C_{10}H_n^{2+}$ with $n = 2$, 5, 6, and 7 and for $C_{11}H_n^{2+}$ with $n = 5$–7, where the maximum population of this channel is observed for $n = 6$. A relatively large abundance of this channel is also found for dication $C_{12}H_2^{2+}$, where it leads to the formation of two symmetrical C_6H^+ products. If the relative rates of fragmentations are inspected together with the relative abundances of CE, we find that charge separation usually occurs for molecules with relatively low fragmentation rates (with exception of ion $C_9H_6^{2+}$). This observation points towards the fact that CE is observed for systems, in which the energy demands for H and H_2 eliminations are relatively high and are thus in the range of the energetically more demanding Coulomb explosion.

The general trends in the fragmentation of medium-sized hydrocarbon dications reported above thus can be roughly summarized in several points: (i) open-shell dications preferentially lose a hydrogen atom, (ii) closed-shell dications prefer to eliminate molecular hydrogen, (iii) for the larger $C_mH_n^{2+}$ dications with $m > 9$, the formation of C_2H_2 can compete with H and H_2 losses, and finally (iv) Coulomb explosion becomes less abundant with increasing size of the parent dication.

The two first points can be demonstrated for the small model systems of $C_3H_n^{2+}$ and $C_4H_n^{2+}$. Fig. 4 shows the dependence of the endothermicities of H and H_2 losses on the number of hydrogen atoms obtained from exploratory DFT calculations. We note in passing that the results shown refer only to the most stable structures found for individual $C_3H_n^{2+}$ and $C_4H_n^{2+}$ dications, and more detailed information can be found in the Supplementary Material. The results demonstrate that the loss of atomic hydrogen is clearly preferred for open-shell dications with some irregularities for dications with a small number of hydrogen atoms. As far as the elimination of molecular hydrogen is concerned, it becomes less energy demanding with increasing number of hydrogen atoms. Thus, based on the computations and experiments it can be tentatively suggested as a rule of thumb that (i) for dications with small number of hydrogen atoms, elimination of H atom will prevail, (ii) for dications with a large number of hydrogen atoms, the H_2-loss channel becomes dominant, and (iii) for dications with medium number of hydrogen atoms, a competition between H and H_2 eliminations will be observed in that open-shell dications will preferentially lose H, whereas closed-shell dications will rather eliminate H_2 molecule.

The experimental results reported above encompass hydrocarbon dications with a small and a medium number of hydrogen atoms and the findings generally agree with the theoretical predictions for the $C_3H_n^{2+}$ and $C_4H_n^{2+}$ model systems. Some data about fragmentations of both closed- and open-shell hydrocarbon dications with a larger number of hydrogen atoms ($C_mH_n^{2+}$ with $m < n$) can be found in the literature and all suggest dominant losses of molecular hydrogen [22,23,32]; this is also in perfect agreement with the tentative model presented here. For example, H_2 loss dominates for $C_6H_8^{2+}$ [22], $C_7H_8^{2+}$ [32], or $C_9H_{11}^{2+}$ [23]. We are aware that our very small model cannot account for all structures and in particular for all possible rearrangements or ring closures followed by the dehydrogenation reactions. However, we believe that within one skeletal arrangement of a hydrocarbon dication, the preference for H or H_2 eliminations will roughly follow the presented scheme. Larger models with six or more carbon atoms lead to an extremely demanding number of possible structures and therefore cannot be applied for the present study.

The trends derived for hydrocarbon dissociations can be used to predict the reactivities of hydrocarbon dications with atomic hydrogen as the most abundant component of interstellar space. Thus, for the $C_mH_n^{2+}$ dications with a large number of hydrogen atoms ($n > m$), the reaction with atomic hydrogen will most probably lead to a depletion of the total number of hydrogen atoms according to reaction (6). Reactions of $C_mH_n^{2+}$ dications with a medium number of hydrogen atoms (n roughly in the range 3 to m) with atomic hydrogen should lead to an enhanced formation of dications with the even number of hydrogen atoms, because dications with even n will react according to reaction (7) and those with odd n according to reaction (6). Finally, no apparent reactivity of $C_mH_n^{2+}$ with n below 3 should be observed (reaction (7)).

$$C_mH_n^{2+} + H \rightarrow C_mH_{n+1}^{2+} \rightarrow C_mH_{n-1}^{2+} + H_2 \qquad (6)$$

$$C_mH_n^{2+} + H \rightarrow C_mH_{n+1}^{2+} \rightarrow C_mH_n^{2+} + H \qquad (7)$$

4. Conclusion

The fragmentation patterns of medium-sized $C_mH_n^{2+}$ dications with $m = 9–14$ and $n = 1–10$ generated from phenanthrene are examined by tandem mass spectrometry. The data reveal several general trends: (i) the major channels correspond to the losses of atomic and molecular hydrogen; (ii) the closed-shell dications with an even number of carbon atoms preferentially eliminate molecular hydrogen, whereas open-shell dications dominantly lose atomic hydrogen; (iii) no similar trends are observed for the dications with an odd number of carbon atoms, most probably because the competition between H and H_2 losses is masked by the occurrence of more energy demanding processes such as acetylene eliminations or even Coulomb explosions; (iv) acetylene elimination is mostly observed for larger dications, which can be related with the larger stability of the fragments compared to the C—C degradation products of smaller hydrocarbon dications; (v) finally, Coulomb explosions are typical for smaller dications; this can be attributed to the lowered stabilities of smaller dications. Exploratory DFT calculations suggest that the alternating preferences for the H and H_2 eliminations from open- and closed-shell dications, respectively, are quite general for $C_mH_n^{2+}$ with medium numbers of hydrogen atoms (n roughly in the range 3 to m); in contrast, dications with $n < 3$ will always preferentially lose a hydrogen atom and for dications with $n > m$, H_2 elimination is expected to dominate.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2008.05.027.

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