

# Reactivity of $C_nH_x^+$ ( $n = 24, 18; x = 0-12$ ) Cluster Ions toward Benzene

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Received December 11, 1998

**Abstract:**  $C_{24}^{*+}$  carbon cluster ions as well as  $C_{24}H_x^+$  and  $C_{18}H_x^+$  cluster ions of low hydrogen content were produced in a FT-ICR spectrometer by repeated losses of  $H^•$  atoms from the molecular ions of coronene  $C_{24}H_{12}$  and of the 4 isomeric polycyclic aromatic hydrocarbons (PAH)  $C_{18}H_{12}$  triphenylene, chrysene, 1,2-benzanthracene, and 2,3-benzanthracene, respectively, using a sequence of SORI-CID procedures. Then, the selected cluster ions were reacted with benzene and benzene- $d_6$  to yield product ions  $[C_nH_x \cdot nC_6H_6]^+$ ,  $n = 1-3$ , and  $[C_nH_{x-1} \cdot nC_6H_6]^+$ . In the latter case it was proven by reaction with  $C_6D_6$  that the  $H^•$  atom lost originates exclusively from the  $C_nH_x$  part of the original cluster ions. In most cases, bimodal kinetics were observed due to a fraction of cluster ions with low or no reactivity toward benzene. The bimolecular rate constants  $k_{bi}$  of the reactions of all reactive cluster ions were determined. For  $C_{24}H_x^+$  ions the  $C_{24}H_{12}^{*+}$  molecular ions of coronene and the  $C_{24}H_{10}^{*+}$  ions do not undergo a reaction with benzene, while for the other  $C_{24}H_x^+$  ions the rate constants increase with decreasing number  $x$  of  $H^•$  atoms but exhibit an odd/even alternation. The even-electron  $C_{24}H_{2m+1}^{*+}$  cations are generally more reactive than the  $C_{24}H_{2m}^{*+}$  odd-electron radical cations. The rate constant of the reaction of benzene with the  $C_{24}^{*+}$  carbon cluster ion eventually produced by SORI-CID from coronene exceeds the rate constant of the same reaction of monocyclic  $C_{24}^{*+}$  carbon cluster ion generated by laser evaporation of graphite by more than 3 orders of magnitude. This shows unambiguously that  $C_{24}^{*+}$  cluster ions of a different structure are generated by the SORI-CID technique. It is suggested that these  $C_{24}^{*+}$  ions retain the graphitic structure of the precursor coronene. This is corroborated by the study of 4 series of  $C_{18}H_x^+$  ions derived from the 4 isomeric PAHs. These ions exhibit analogous and as characteristic reactions with benzene as the  $C_{24}H_x^+$  ions, but the rate constants of individual  $C_{18}H_x^+$  ions are different for the 4 isomeric precursor PAHs. This indicates very strongly that all these  $C_nH_x^+$  ions produced by repeated losses of  $H^•$  atoms from ionized PAHs with a sequence of SORI-CID procedures retain the graphitic structures of the precursor molecules.

## 1. Introduction

The chemistry of carbon clusters has been of broad interest during the past decades,<sup>1,2</sup> even before the discovery<sup>3</sup> and synthesis<sup>4</sup> of macroscopic amounts of fullerenes. The general method used to synthesize fullerenes is the arc-discharge of graphite.<sup>4a,b</sup> However, as for the generation of small carbon

clusters up to 30 atoms, high-frequency spark evaporation,<sup>5</sup> thermal evaporation of carbon,<sup>6</sup> combustion,<sup>7</sup> secondary ion mass spectrometry,<sup>8</sup> laser evaporation,<sup>9</sup> and electron impact-induced elimination of all Cl atoms from perchlorinated polycyclic aromatic hydrocarbons (PAH)<sup>10,11</sup> were reported. A remarkable design of a pulsed laser vaporization source coupled with a supersonic expansion using an inert carrier gas was shown to generate carbon clusters having up to several hundreds of atoms.<sup>3,12</sup> However, due to the limitation to combine some of these techniques with a mass spectrometer or a similar device,

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only the laser evaporation of graphite and dechlorination of perchloroarenes by electron impact have been used to prepare carbon cluster ions  $C_n^{*+}$  for studying their ion/molecule reactions.,<sup>1b,3b,11,13-18</sup>

In particular, the structures and reactivities of carbon clusters were the subject of an extensive research effort. Reactivity studies,<sup>12,16a</sup> photoelectron spectra,<sup>19</sup> metastable dissociation in a mass spectrometer,<sup>20</sup> and computational studies<sup>21</sup> provided information about the structures of carbon clusters. Systematic studies of the structures of carbon cluster ions in the range of  $C_5$ – $C_{80}$  have been reported by Bowers et al.<sup>2,22</sup> and Jarrold et al.<sup>23</sup> using the method of ion chromatography.<sup>24</sup> From these studies it is agreed that small  $C_n^{*+}$ ,  $n < 10$ , clusters form only linear carbon chains. Around  $C_{10}^{*+}$  monocyclic rings appear and from  $C_{11}^{*+}$  to  $C_{27}^{*+}$  the monocyclic ring is either the only structure or at least highly predominant. Near  $C_{20}^{*+}$  planar ring systems are formed followed by bicyclic, tricyclic, and tetracyclic structures for  $C_n^{*+}$ ,  $n = 30$ –40. Finally, the first cage fullerene is observed at  $C_{30}^{*+}$ , and these species become dominant<sup>2</sup> beyond  $C_{50}^{*+}$ . It should be noted, however, that these results reflect the situation of carbon cluster formation by laser evaporation of graphite. Thus, a reasonable explanation<sup>23,25</sup> for the preference of the observed structures under these conditions is that the growth of carbon clusters in a laser plasma is kinetically controlled, and that small linear  $C_n^{*+}$  can isomerize easily into monocyclic rings, which rearrange further to bicyclic, tricyclic structures without large energy barriers.

Theoretical calculations predict that for carbon clusters and their radical cations containing more than 20 C atoms other structures may be at least as stable as those observed during laser evaporation. In particular, planar graphitic structures composed only of six-membered rings can compete with planar mono- and bicyclic structures, and curved graphitic structures with five- and six-membered rings or even fullerenes were calculated also to be stable species for  $C_n^{*+}$  of this cluster size.<sup>21d,26</sup> However, planar graphitic structures were only observed at about  $C_{29}^{*+}$ <sup>2,22-c,27</sup> and continued to be present until  $C_{60}^{*+}$ , while curved graphitic structures were absent at any cluster size. This indicates that laser evaporation very likely produce only a selection of the possible structures of carbon cluster ions.

Anyway, studies of the reactivities of  $C_n^{*+}$ ,  $10 \leq n \leq 24$ , carbon clusters both from electron impact-induced elimination of Cl atoms of perchlorinated PAHs<sup>11</sup> and from laser evaporation of graphite,<sup>18b</sup> gave identical results and suggest that monocyclic  $C_n^{*+}$  were produced also from the polycyclic perchloroarenes by electron impact ionization. This might be due to the high energy necessary to eliminate all chloro substituents for the PAHs,<sup>11</sup> since this energy has to be imparted onto the molecule during the initial electron impact ionization. This is corroborated by a recent study<sup>28</sup> searching for graphitic isomers generated from decachloroacene,  $C_{12}Cl_{10}$ , by electron impact ionization. Although the polycyclic structure of the parent PAH was retained in  $C_{12}Cl_x^+$  cluster ions formed by loss of Cl substituents down to  $C_{12}Cl_4^+$ , the only structure of  $C_{12}^{*+}$  eventually generated by elimination of all 10 Cl atoms was the monocyclic ring. In contrast, a previous study of our laboratory<sup>29</sup> indicated that  $C_{24}^{*+}$  carbon cluster ions of a graphitic structure might have been formed as an isomer coexisting with the monocyclic cluster from perchlorocoronene  $C_{24}Cl_{12}$  using the technique of multiple-excitation collisional activation (MECA) of Fourier transform ion-cyclotron resonance (FT-ICR) spectrometry. Since at least some of the  $C_{24}^{*+}$  cluster ions created by this technique arise by a more "soft" mode of sequential Cl elimination and re-excitation, this would indicate that carbon cluster ions of the missing graphitic structures can be generated by a step-by-step elimination of substituents from the rim of a PAH molecule.

In our previous study<sup>30</sup> about the generation of  $C_n^{*+}$  carbon cluster ions and corresponding hydrogenated  $C_nH_x^+$  species of low hydrogen content, this new approach was achieved using the sustained off-resonance irradiation (SORI) method and collision-induced dissociation (CID) technique available in FT-ICR spectrometry for a stepwise elimination of hydrogen atoms from the molecular ions of selected PAHs. The SORI-CID<sup>31</sup> is a collisional activation method, which excites the ions slightly by off-resonance irradiation in a collision bath gas present in the FT-ICR cell. As a consequence, the selected ions are continually excited and de-excited, so that the excess energy

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of the ions is accumulated only slowly by collisions with the bath gas until the threshold for the fragmentation of lowest activation energy is reached.<sup>32</sup> Since the fragment ions are not excited any more, SORI-CID usually yields only the products of the low-energy fragmentation with high efficiency.<sup>31a</sup> For the molecular ions and fragment ions of many PAHs the loss of a  $H^+$  atom is the process of lowest activation energy. As a result we showed that  $C_n^{*+}$  carbon cluster ions as well as partially hydrogenated  $C_nH_x^+$ ,  $n = 13-24$  and  $x = 0-11$ , species were formed with distinct abundances by SORI-CID starting with the molecular ions of a PAH and removing its  $H^+$  atoms step-by-step. In view of this "tailored" mode of generation of carbon cluster ions by the SORI-CID method and of the importance<sup>33</sup> of lowly hydrogenated  $C_nH_x$  carbon clusters in astrochemistry<sup>34</sup> and combustion processes,<sup>3b,7,35</sup> the investigation of the structures and the reactions of this kind of  $C_n^{*+}$  and  $C_nH_x^+$  cluster ions will be of great interest.

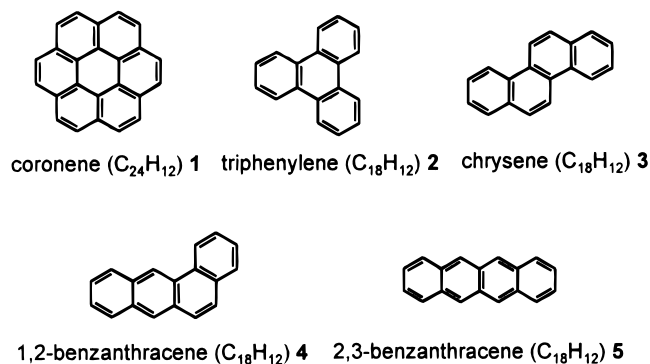
In this paper, we report results of the study of the gas-phase reactions of benzene with a series of  $C_{24}H_x^+$  ions,  $x = 0-12$ , and  $C_{18}H_x^+$ ,  $x = 4-12$ , generated by eliminating  $H^+$  atoms with the SORI-CID technique from the molecular ions of coronene  $C_{24}H_{12}$  and 4 isomeric PAH  $C_{18}H_{12}$ , respectively. It has been shown previously<sup>30</sup> that in the case of coronene  $C_{24}^{*+}$  carbon cluster ions can be prepared by SORI-CID with an abundance sufficient for kinetic studies. This gives the opportunity to observe the dependence of the reactivity on hydrogen content of  $C_{24}H_x^+$  for the complete series and to compare the results with earlier studies<sup>18</sup> of the reaction of benzene with  $C_{24}^{*+}$  generated by laser evaporation. These investigations can give information about possible structural changes along the series of  $C_{24}H_x^+$  ions by abrupt changes of their reactivity. In the second part of the results about the reactivities of a series of  $C_{18}H_x^+$ ,  $4 \leq x \leq 12$ , ions derived from 4 isomeric  $C_{18}H_{12}$  toward benzene are reported. In the case of smaller PAHs we were not successful<sup>30</sup> in preparing  $C_n^{*+}$ ,  $n < 20$ , carbon cluster ions by SORI-CID. However, the study of 4 series of isomeric  $C_{18}H_x^+$  ions can show whether they will retain their individual reactivity down to the lowest number of hydrogen atoms present in the clusters, and thus will give again information about changes of the graphitic structures of the ionized parent molecules during the repeated losses of hydrogen atoms.

## 2. Experimental Section

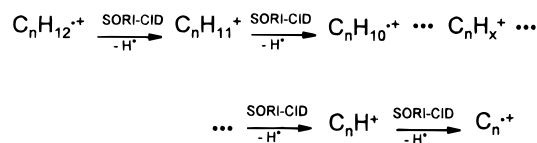
All experiments were carried out using a Bruker CMS 47X FT-ICR spectrometer equipped with a 4.7 T superconducting magnet, an Infinity Cell,<sup>36</sup> and an external electron ionization (EI) source.<sup>37</sup> All compounds employed were commercially available in pure form and were used without further purification.

**Preparation of  $C_nH_x^+$  Cluster Ions.** The details of the preparation of the  $C_nH_x^+$  cluster ions by SORI-CID of the molecular ions of the

### Scheme 1



### Scheme 2



PAHs coronene ( $C_{24}H_{12}$ , 1), triphenylene ( $C_{18}H_{12}$ , 2), chrysene ( $C_{18}H_{12}$ , 3), 1,2-benzanthracene ( $C_{18}H_{12}$ , 4), and 2,3-benzanthracene ( $C_{18}H_{12}$ , 5) (all structures shown in Scheme 1) have been described previously.<sup>30</sup> To perform ion/molecule reactions the neutral reactant, i.e., benzene and benzene- $d_6$  in this study, was kept at a constant background pressure within the FT-ICR cell during the complete procedure. Briefly, the molecular ions of PAHs generated in the external EI source by the 30 eV electron ionization were transferred into the FT-ICR cell and isolated by the standard procedures of ejection of all unwanted ions by a broad band radio frequency (rf) pulse and a series of single shot (SS) rf pulses. Then, the SORI-CID<sup>31</sup> was applied to these ions by setting an "off-resonance" irradiation pulse, where the frequency was set 150–380 Hz aside from the natural cyclotron frequency of the selected ions. The duration of the pulse was given by  $m/(\nu_0 - \nu)$ , where  $\nu_0$  (in Hz) is the ion cyclotron frequency of the selected ion, and  $\nu$  (in Hz) corresponds to the irradiation frequency, which was set always a certain number of hertz lower (the corresponding  $m/z$  value is at the side higher in mass) than  $\nu_0$  to avoid possible excitation of the  $[M - H]^+$  product ions. The integral number  $m$  stands for the number of acceleration/deceleration cycles during SORI and was usually between 2 and 6. A pulse of argon gas was admitted to the cell as the target gas for collisional activation by a pulsed magnetic valve with a peak pressure of about  $10^{-5}$  mbar. With this method, ions could be irradiated for long periods of time to undergo multiple collisions with the bath gas and dissociate efficiently by the lowest energy pathway, i.e., elimination of one  $H^+$  atom in most cases studied here. By applying again an analogous SORI-CID procedure to the  $[M - H]^+$  product ions,  $[M - 2H]^+$  ions were produced, and so on as delineated in Scheme 2.

After a series of SORI-CID experiments, the  $C_nH_x^+$  cluster ions, which were expected to be chosen for the reactivity study, were formed and isolated by the procedures described above. Special care has to be taken to optimize the parameters of SORI-CID with respect to minimal loss and excitation to the selected  $C_nH_x^+$  ions. Generally, at least under our experimental conditions, the  $C_nH_x^+$  ions formed by SORI-CID and subsequently isolated are already thermalized. However, to remove any unintended excitation of the selected  $C_nH_x^+$  ions, a pulsed magnetic valve was opened for 15 ms to admit a pressure pulse of Ar (peak pressure ca.  $10^{-5}$  mbar) into the FT-ICR cell for 1–2 s to thermalize the  $C_nH_x^+$  ions. This was followed by SS ejections to remove any reaction product ions formed during this time, for example by charge and/or proton transfer.

**Ion/Molecule Reactions.** Following the procedure for generating/isolating the  $C_nH_x^+$  cluster ions, these ions were allowed to react with the neutral reactant present in the ICR cell at a constant background pressure of about  $(2-80) \times 10^{-8}$  mbar at 300 K. The experimental rate constants  $k_{\text{exp}}$  of the ion/molecule reactions were determined by recording the decay of the intensity of the  $C_nH_x^+$  ions and the rise of the product ions as a function of the reaction time, and by fitting these

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experimental kinetic plots using the Origin PC program.<sup>38</sup> The bimolecular rate constants  $k_{\text{bi}}$  were calculated from  $k_{\text{exp}}$  by taking into account the number density of the neutral reactant in the FT-ICR cell derived from the partial pressure. The reaction efficiency (eff %) was obtained from the ratio of the experimental  $k_{\text{bi}}$  and the theoretical collision constant  $k_{\text{ado}}$ , which was calculated according to the method of Su and Chesnavich.<sup>39</sup> The rate constants reported are estimated to be accurate within 20%, and the main error is due to the measurement of the partial pressure of the neutral reactant.

The pressure within the FT-ICR cell was measured by an ion gauge close to the high-vacuum pump of the cell. The pressure reading was calibrated by rate measurements of the reactions  $\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \cdot\text{CH}_3$  ( $k_{\text{bi}} = 1.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>40</sup>) and  $\text{NH}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \cdot\text{NH}_2$  ( $k_{\text{bi}} = 2.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>41</sup>) as described before<sup>11a</sup> and corrected by the sensitivity constants of the reactants with a standard method.<sup>42</sup>

**CID of the Product Ions.** To obtain information about the product ion structures of the ion/molecule reactions of  $\text{C}_n\text{H}_x^+$  with the benzene or benzene- $d_6$ , SORI-CID of the product ions was achieved generally with the same procedure as described above. However, in this case the neutral reactant was introduced as a pressure pulse into the cell for reaction with the isolated  $\text{C}_n\text{H}_x^+$  ion. After a certain reaction time the neutral reactant was pumped away and the product ion of interest was isolated. Then, SORI-CID was applied to the product ion by slightly adjusting the excitation energy until at least half of the target ion had dissociated. Finally, all ions were detected in the standard mode. There are two advantages of using SORI-CID rather than the normal CID to investigate the product ion structures. First, the high dissociation efficiency of SORI-CID allows the study of product ions of low intensity, and second, the "soft" excitation mode of SORI-CID makes it possible to observe mainly the dissociation pathway of lowest energy. For the kind of product ions studied here, this provides positive structural information.

### 3. Results and Discussion

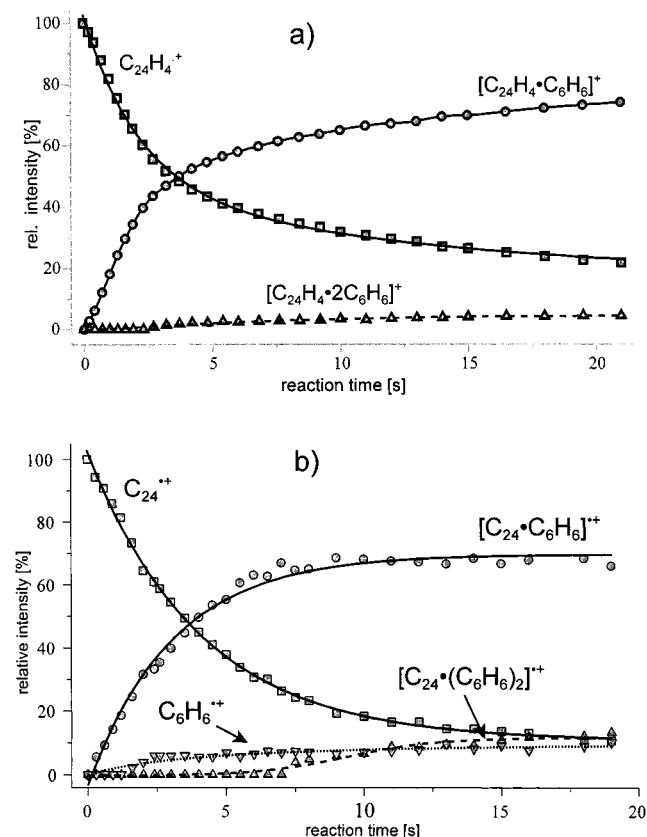
**3.1.  $\text{C}_{24}\text{H}_x^+$  Cluster Ions.** By means of SORI-CID, the series of  $\text{C}_{24}\text{H}_x^+$  ( $x = 0-12$ ) cluster ions were generated with large abundance from coronene **1**. During these experiments it was observed that a background pressure of benzene (the neutral reactant) improved the efficiency of the SORI-CID processes, most likely because collisions with benzene were cooling the ions rather effectively which kept them from escaping from the center of the FT-ICR cell. Nevertheless, it is remarkable that even the pure carbon cluster ion  $\text{C}_{24}^{*+}$  was produced by eliminating 12  $\text{H}^{\bullet}$  atoms from the molecular ions of **1** with sufficient intensity for the following study of ion/molecule reactions with benzene and benzene- $d_6$ .

**Reactions of  $\text{C}_{24}\text{H}_x^+$ ,  $x = 0-12$ , with Benzene.** The products, branching ratios, rate constants  $k_{\text{bi}}$ , and reaction efficiencies of the reaction of  $\text{C}_{24}\text{H}_x^+$  ( $x = 0-12$ ) cluster ions with benzene are given in Table 1. As an example, the plots of the ion intensity as a function of the reaction time ("kinetic plot") are shown in Figure 1 for the reaction of  $\text{C}_{24}\text{H}_4^{*+}$  and of  $\text{C}_{24}^{*+}$  with benzene. In most cases a bimodal reactivity was observed, and the experimental kinetic plot could be fitted by assuming a fraction of  $\text{C}_{24}\text{H}_x^+$  ( $x = 0-12$ ) cluster ions reacting by pseudo-first-order kinetics while the remaining fraction reacts much more slowly or does not react at all with benzene during the time scale of the experiment. The pseudo-first-order kinetics obtained for the reactive fraction of ions is very strong evidence

**Table 1.** Bimolecular Rate Constants,  $k_{\text{bi}}$ , and Branching Ratio of the Ion/Molecule Reaction of  $\text{C}_{24}\text{H}_x^+$ ,  $x = 0-12$ , with Benzene

cluster ion $\text{C}_{24}\text{H}_x^+$	branching ratio			$k_{\text{bi}}^a$	eff (%) = $k_{\text{bi}}/k_{\text{ado}}^c$
	addition	add./elimin	unreactive		
$\text{C}_{24}\text{H}_{12}^{*+}$	no reaction			100	
$\text{C}_{24}\text{H}_{11}^{*+}$	93		7	0.78	8.2
$\text{C}_{24}\text{H}_{10}^{*+}$	no reaction			100	
$\text{C}_{24}\text{H}_9^{*+}$	72	6	22	0.52	5.5
$\text{C}_{24}\text{H}_8^{*+}$	29		71	0.11	1.2
$\text{C}_{24}\text{H}_7^{*+}$	78	3	19	0.54	5.6
$\text{C}_{24}\text{H}_6^{*+}$	59		41	0.30	3.2
$\text{C}_{24}\text{H}_5^{*+}$	84	3	13	1.54	16
$\text{C}_{24}\text{H}_4^{*+}$	75		25	0.88	9.2
$\text{C}_{24}\text{H}_3^{*+}$	89	6	5	4.07	42
$\text{C}_{24}\text{H}_2^{*+}$	83		17	3.32	35
$\text{C}_{24}\text{H}^{*+}$	86	11	3	7.83	82
$\text{C}_{24}^{*+}$	79		11	8.02	84

<sup>a</sup>  $\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>b</sup> The charge transfer is about 10%. <sup>c</sup> Calculated by the method of ref 39.



**Figure 1.** Kinetic plots for the reactions of (a)  $\text{C}_{24}\text{H}_4^{*+}$  with benzene ( $p_{\text{benzene}} = 20.8 \text{ mbar}$ ) and (b)  $\text{C}_{24}^{*+}$  with benzene ( $p_{\text{benzene}} = 1.9 \text{ mbar}$ ).

that reactions of ions without excess energy were studied. Further, the reactive  $\text{C}_{24}\text{H}_x^+$  ions generated by eliminating  $\text{H}^{\bullet}$  atoms using SORI-CID from PAHs are either homogeneous in structure so that they exhibit naturally identical rate constants or, more likely, are a mixture of reactive isomers which do not differ significantly in their reactivity. This latter result could be the case if the reaction with benzene occurs always at a local reaction center common to all ions, for example at a carbenium center. Since all  $\text{C}_{24}\text{H}_x^+$  ions can be viewed as modified aryl cations, this is a plausible possibility. The reaction efficiency for the reactive fraction of the ions is always lower than 85%. Therefore, the reactions rates are not controlled by the collision of the  $\text{C}_{24}\text{H}_x^+$  ion with a benzene molecule but by a rate determining step later on the reaction coordinate. Considering the appearance of a fraction of  $\text{C}_{24}\text{H}_x^+$  ions unreactive toward

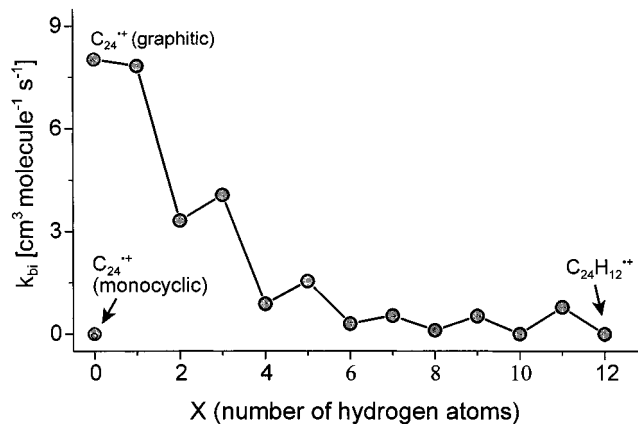
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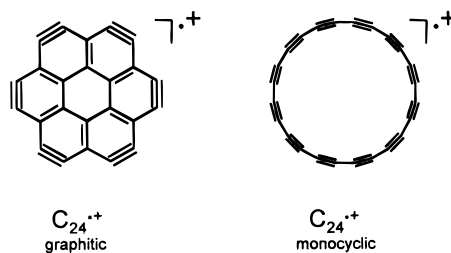


**Figure 2.** Variation of the rate constant  $k_{bi}$  of the reaction of  $C_{24}H_x^+$  cluster ions and benzene with the number  $x$  of hydrogen atoms ( $k_{bi}$  for  $C_{24}^{2+}$  from ref 18).

benzene, it has to be taken into account that the kinetic experiments discussed here are very demanding and that a small amount (<5%) of unreactive species may be an artifact due to experimental difficulties and the curve-fitting procedure. Nevertheless, in most cases the amount of the unreactive component is too large to be an artifact. This is mainly observed for  $C_{24}H_x^{2+}$  radical ions with  $x = 2m$  corresponding to an even number, and the amount of unreactive isomers decreases with decreasing  $x$ . This suggests that the unreactive  $C_{24}H_{2m}^{2+}$  radical ions exhibit a unique structure element, and one possible explanation is an aryne structure generated by loss of 2  $H^\bullet$  atoms from two neighboring positions. This results in a  $C_{24}H_{2m}^{2+}$  ion in which the positive charge and the radical site are delocalized in the aromatic  $\pi$ -electron system as in the original PAH and which is not very reactive. In contrast, the  $C_{24}H_{2m+1}^{2+}$  cations must expose an empty  $\sigma$ -bonding orbital within the plane of the PAH which makes them analogues of the reactive phenyl cation. An additional and related argument to explain the occurrence of unreactive isomers in particular for  $C_{24}H_{2m}^{2+}$  and the decrease of this fraction with decreasing number of  $H^\bullet$  atoms in the ions is that the reaction of benzene with the  $C_{24}H_{2m+1}^{2+}$  cations is expected to be more exothermic than that with the  $C_{24}H_{2m}^{2+}$  radical cations, and that in both series of ions the reactivity of all isomers should increase with increasing unsaturation of the  $C_{24}H_x^+$  cluster ions.

**Rate Constants of  $C_{24}H_x^+$ ,  $x = 0-12$ .** The rate constants for the ion/molecule reactions of  $C_{24}H_x^+$ ,  $x = 0-12$ , with benzene are plotted in Figure 2 versus the number of  $H^\bullet$  atoms in the  $C_{24}H_x^+$  cluster ions. Generally, the reactivity increases with decreasing numbers of  $H^\bullet$  atoms, but it is obvious that an odd/even modulation of the reactivity occurs throughout this series of ions. The  $C_{24}H_x^+$  ions with  $x = 2m + 1$  corresponding to an odd number of  $H^\bullet$  atoms include a closed shell of valence electrons such as a carbenium ion and are more reactive toward benzene than the corresponding  $C_{24}H_x^{2+}$  radical cations with  $x = 2m$  corresponding to an even number of  $H^\bullet$  atoms. The molecular ion  $C_{24}H_{12}^{2+}$  of coronene does not react with benzene, while the  $C_{24}H_{11}^+$  ion, formed by loss of any one of the 12  $H^\bullet$  atoms, exhibits a reaction efficiency of 8.2%. Unexpectedly, the  $C_{24}H_{10}^{2+}$  ion exhibits no reactivity toward benzene, although it is derived by further loss of a  $H^\bullet$  atom from the reactive  $C_{24}H_{11}^+$  ion. This suggests the loss of the second  $H^\bullet$  atom from  $C_{24}H_{11}^+$  from the neighboring position to the first loss and a stabilization of the resulting  $C_{24}H_{10}^{2+}$  by an "aryne" triple bond. In these "aryne radical cations" the positive charge and the radical site are delocalized in the  $\pi$ -electron system as in the

### Scheme 3



original coronene molecular ion, which is also unreactive. The  $C_{24}H_x^+$  ions followed by elimination of additional  $H^\bullet$  atoms down to  $C_{24}H_6^{2+}$  exhibit medium reactivity, but the reactivity of cluster ions containing a smaller number of  $H^\bullet$  atoms increases steeply. Excluding the unreactive  $C_{24}H_{12}^{2+}$  and  $C_{24}H_{10}^{2+}$ , the rate constants for the other  $C_{24}H_x^+$  ions cover a range of a factor of 73 from  $k_{bi} = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reactions of  $C_{24}H_8^{2+}$  to that of  $k_{bi} = (8.0 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $C_{24}^{2+}$ .

The high reactivity of the carbon cluster ions  $C_{24}^{2+}$ , besides a rather small fraction of an unreactive isomer, generated in this work by SORI-CID with benzene is significant. The rate constant  $k_{bi} = (8.02 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  corresponds to a reaction efficiency of 84%, so that the reaction nearly approaches the collision controlled rate limit. Previous studies of the reaction of a  $C_{24}^{2+}$  ion formed by laser evaporation of graphite<sup>18a,b</sup> or electron ionization (EI) of perchlorocoronene  $C_{24}Cl_{12}$ <sup>29</sup> show that this monocyclic  $C_{24}^{2+}$  exhibits an extremely low reactivity toward benzene. The rate constant  $k_{bi}$  was reported<sup>18a,b</sup> to be less than  $2.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Therefore, the reactivity of the  $C_{24}^{2+}$  carbon cluster ion studied here exceeds that of monocyclic  $C_{24}^{2+}$  by more than a factor of  $3 \times 10^3$ ! This substantial difference of the reactivity between these two kinds of  $C_{24}^{2+}$  carbon cluster ions is clearly indicative of absolutely different structures. A notably reactive isomer of  $C_{24}^{2+}$  carbon cluster ions was also reported recently by our group<sup>29</sup> using the MECA technique for carbon cluster ion preparation from  $C_{24}Cl_x^+$  ions with  $x = 1-12$ . An isomeric component  $C_{24}^{2+}$ , which is more reactive and behaves differently toward pyridine than monocyclic  $C_{24}^{2+}$ , was observed, and it was suggested that this reactive species of  $C_{24}^{2+}$  still has the graphitic carbon skeleton of coronene **1** (Scheme 3). However, under the conditions used in that study, MECA may plausibly produce a mixture of isomeric  $C_{24}^{2+}$ .

An important difference between monocyclic carbon cluster ions and their graphitic isomers shown in Scheme 3 is the very different MO system of the  $\pi$ -electrons. The monocyclic carbon cluster ions exhibit two delocalized  $\pi$ -electron systems, one by overlap of the 2p carbon AO perpendicular to the plane of the ring and a second one by overlap within the plane of the ring. In contrast, the graphitic carbon cluster ions contain only one delocalized  $\pi$ -electron system, that of the corresponding PAH, and at the rim of the plane each pair of  $sp^2$  AO of neighboring C atoms combine to a localized C-C aryne bond. Since the positive charge and the radical site are expected to reside in one of these localized aryne bonds, these graphitic carbon cluster ions should be more reactive than the monocyclic isomer.

The  $C_{24}^{2+}$  and  $C_{24}H_x^+$ ,  $x = 1-11$ , ions studied here were generated in a more gentle manner by SORI-CID which should favor carbon cluster formation without a deep-seated rearrangement of the carbon skeleton of the precursor molecules if this results in a stable cluster structure. The observation of a highly reactive  $C_{24}^{2+}$  species agrees with this expectation. Unfortunately, an investigation of the ion/molecule reactions of this

**Table 2.** Products of the Reaction of  $C_{24}H_x^+$ , from Coronene **1**, with  $C_6D_6$  and Their Fragments of SORI-CID

cluster ion	product ions	branching ratio (%) <sup>a</sup>	fragments of SORI-CID	
			ion + neutrals <sup>b</sup>	rel int (%) <sup>c</sup>
$C_{24}H_{12}^{*+}$	no reaction			
$C_{24}H_{11}^+$	$[C_{24}H_{11}\cdot C_6D_6]^+$	94	$[C_{24}H_{10}\cdot C_6D_6]^+ + H\cdot$	100
$C_{24}H_{10}^{*+}$	no reaction			
$C_{24}H_9^+$	$[C_{24}H_9\cdot C_6D_6]^+$	36	$[C_{24}H_8\cdot C_6D_6]^{*+} + H\cdot$	100
	$[C_{24}H_9\cdot(C_6D_6)_2]^+$	36	$[C_{24}H_8\cdot(C_6D_6)_2]^{*+} + H\cdot$	100
	$[C_{24}H_8\cdot C_6D_6]^{*+}$	7		
$C_{24}H_8^{*+}$	$[C_{24}H_8\cdot C_6D_6]^{*+}$	29		
$C_{24}H_7^+$	$[C_{24}H_7\cdot C_6D_6]^+$	35	$[C_{24}H_6\cdot C_6D_6]^{*+} + H\cdot$	77
			$[C_{24}H_4\cdot C_6D_6]^{*+} + 3H\cdot$	23
	$[C_{24}H_7\cdot(C_6D_6)_2]^+$	38	$[C_{24}H_6\cdot(C_6D_6)_2]^{*+} + H\cdot$	100
	$[C_{24}H_7\cdot(C_6D_6)_3]^+$	7		
	$[C_{24}H_6\cdot C_6D_6]^{*+}$	3		
$C_{24}H_6^{*+}$	$[C_{24}H_6\cdot C_6D_6]^{*+}$	55	$[C_{24}H_5\cdot C_6D_6]^+ + H\cdot$	40
			$[C_{24}H_4\cdot C_6D_6]^{*+} + 2H\cdot$	10
			$[C_{24}H_3\cdot C_6D_6]^+ + 3H\cdot$	50
	$[C_{24}H_6\cdot(C_6D_6)_2]^{*+}$	4		
$C_{24}H_5^+$	$[C_{24}H_5\cdot C_6D_6]^+$	47	$[C_{24}H_4\cdot C_6D_6]^{*+} + H\cdot$	100
	$[C_{24}H_5\cdot(C_6D_6)_2]^+$	24		
	$[C_{24}H_5\cdot(C_6D_6)_3]^+$	14		
	$[C_{24}H_4\cdot C_6D_6]^{*+}$	3		
$C_{24}H_4^{*+}$	$[C_{24}H_4\cdot C_6D_6]^{*+}$	73	$[C_{24}H_3\cdot C_6D_6]^+ + H\cdot$	24
			$[C_{24}H_2\cdot C_6D_6]^{*+} + 2H\cdot$	38
			$[C_{24}H\cdot C_6D_6]^+ + 3H\cdot$	38
	$[C_{24}H_4\cdot(C_6D_6)_2]^{*+}$	2		
$C_{24}H_3^+$	$[C_{24}H_3\cdot C_6D_6]^+$	57	$[C_{24}H_2\cdot C_6D_6]^{*+} + H\cdot$	77
			$[C_{24}H\cdot C_6D_6]^+ + 2H\cdot$	23
	$[C_{24}H_3\cdot(C_6D_6)_2]^+$	23		
	$[C_{24}H_3\cdot(C_6D_6)_3]^+$	9		
	$[C_{24}H_2\cdot C_6D_6]^{*+}$	6		
$C_{24}H_2^{*+}$	$[C_{24}H_2\cdot C_6D_6]^{*+}$	75		
	$[C_{24}H_2\cdot(C_6D_6)_2]^{*+}$	8		
$C_{24}H^+$	$[C_{24}H\cdot C_6D_6]^+$	61	$[C_{24}\cdot C_6D_6]^{*+} + H$	100
	$[C_{24}H\cdot(C_6D_6)_2]^+$	26		
	$[C_{24}\cdot C_6D_6]^{*+}$	11		
$C_{24}^{*+}$	$[C_{24}\cdot C_6D_6]^{*+}$	66		
	$[C_{24}\cdot(C_6D_6)_2]^{*+}$	13		

<sup>a</sup> The branching ratio (in %) was determined at the end of the reaction, and the unreactive and small amount of the charge transfer (only for  $C_{24}^{*+}$ ) are not shown here. <sup>b</sup> The losses of two or more  $H\cdot$  atoms may also result in  $H_2$ ; however, in the case of SORI-CID studied here, consecutive losses of  $H\cdot$  are more likely. <sup>c</sup> In percentage of the total fragment ion intensity.

$C_{24}^{*+}$  with pyridine failed due to the quick loss of the  $C_{24}H_x^+$  ion intensity during the ion preparation by proton transfer to pyridine. Nonetheless, the regular increase of the reactivity of the  $C_{24}H_x^+$  ions with decreasing numbers of  $H\cdot$  atoms present in the cluster ions can be taken as strong evidence for a graphitic structure of the present  $C_{24}^{*+}$ . This dependence of reactivity on hydrogen content can be explained either by structural changes of the carbon skeleton occurring gradually with  $H\cdot$  loss or, much more likely, by no changes of the carbon skeleton but by a reactivity continuously increasing with increasing unsaturation. This would imply a graphitic structure of the  $C_{24}^{*+}$  carbon cluster ion prepared by SORI-CID from ionized coronene **1**.

**Structure of Product Ions.** In this connection an analysis of the structure of the product ions of the reaction of benzene with the  $C_{24}H_x^+$  ions becomes important. This has been performed by using benzene-*d*<sub>6</sub> as reactant and by SORI-CID of the relevant product ions. The product ions formed with benzene and benzene-*d*<sub>6</sub> are listed in Tables 1 and 2, respectively.

It is noticeable that an odd/even regularity appears here also by observing two types of reaction pathways. One pathway which is common to all reactive  $C_{24}H_x^+$  ions is the addition of one or more molecules of benzene to form  $[C_{24}H_x\cdot(C_6H_6)_y]^{*+}$  adduct ions. For  $C_{24}H_9^+$ ,  $C_{24}H_6^{*+}$ ,  $C_{24}H_4^{*+}$ ,  $C_{24}H_2^{*+}$ ,  $C_{24}H^+$ ,

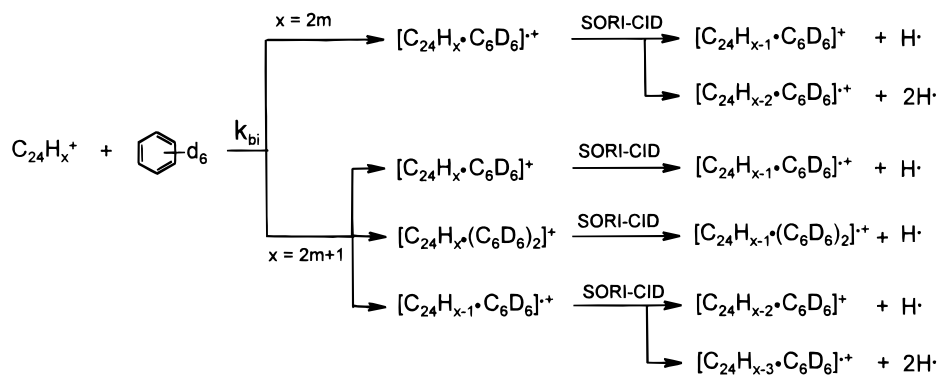
and  $C_{24}^{*+}$  up to two benzene molecules and for  $C_{24}H_7^+$ ,  $C_{24}H_5^+$ , and  $C_{24}H_3^+$  up to three benzene molecules were observed to add to  $C_{24}H_x^+$ . This addition is the only pathway for  $C_{24}H_x^+$ ,  $x = 2m$ , radical cations with an even number of  $H\cdot$  atoms. The other reaction pathway is an addition-elimination sequence by addition of a benzene molecule followed by elimination of one  $H\cdot$  atom, which is exclusively observed for even-electron  $C_{24}H_x^+$ ,  $x = 2m + 1$ , cations containing an odd number of  $H\cdot$  atoms. The  $H\cdot$  atom lost originates from that part of the adduct ions which comes from  $C_{24}H_x^+$  rather than from benzene, so that  $[C_{24}H_{x-1}\cdot C_6H_6]^{*+}$  product ions are formed. This is proven by the reactions with benzene-*d*<sub>6</sub> as shown in Table 2. The odd/even alternating reaction pathways were observed throughout this series of ions with the exception of  $C_{24}H_{11}^+$ , which shows only the addition of one benzene molecule without  $H\cdot$  loss. However, the loss of one  $H\cdot$  atom from the  $[C_{24}H_{11}\cdot C_6D_6]^+$  product ion is the predominant SORI-CID process. Anyway, the fact that both the reactivity and the reaction pathways show the characteristic odd/even regularity throughout the whole series may indicate no rigorous structural changes from  $C_{24}H_{12}^{*+}$  to  $C_{24}^{*+}$  besides the alternation between an odd and even number of valence electrons.

SORI-CID studies were carried out for some of the product ions to obtain information about the bonding of benzene-*d*<sub>6</sub> in the product ions of the primary and secondary reactions. The ions studied, the CID product ions, and their relative abundance are also summarized in Table 2. It is immediately apparent that no loss of benzene-*d*<sub>6</sub> is observed from any of the primary and secondary product ions, even at higher excitation energy. This indicates that the benzene molecules are added to  $C_{24}H_x^+$  by forming new C-C bonds rather than by simple electrostatic association. It is striking that, without exception, all fragmentations occur at that part of the product ion which stems from the original cluster ion as shown in Scheme 4.

The loss of one  $H\cdot$  atom is the predominant dissociation reaction for the primary product ions of the type  $C_{24}H_x^+$ ,  $x = 2m + 1$  ( $[C_{24}H_{11}\cdot C_6D_6]^+$ ,  $[C_{24}H_9\cdot C_6D_6]^+$ ,  $[C_{24}H_7\cdot C_6D_6]^+$ ,  $[C_{24}H_5\cdot C_6D_6]^+$ ,  $[C_{24}H_3\cdot C_6D_6]^+$ , and  $[C_{24}H\cdot C_6D_6]^+$ ), yielding  $[C_{24}H_{2m}\cdot C_6D_6]^{*+}$  fragment ions. It is of interest to note that  $[C_{24}H_{2m}\cdot C_6D_6]^{*+}$  ions derived by loss of  $H\cdot$  from the primary  $[C_{24}H_{2m+1}\cdot C_6D_6]^+$  product ions by CID behave identically to the corresponding primary product radical cations obtained directly by reaction with benzene-*d*<sub>6</sub>. This is a further indication that all  $C_{24}H_x^+$  ions are closely related in their structure, which is most easily understood by retaining the graphitic carbon skeleton of coronene **1** in all these ions. Most of the secondary  $[C_{24}H_x\cdot(C_6D_6)_2]^{*+}$  product ions could not be examined by SORI-CID due to insufficient intensity. Two of them,  $[C_{24}H_9\cdot(C_6D_6)_2]^+$  and  $[C_{24}H_7\cdot(C_6D_6)_2]^+$ , which could be analyzed, behave identically to the primary product ions and exhibit loss of one  $H\cdot$  atom as the only fragmentation process. In particular, no loss of benzene-*d*<sub>6</sub> was detected. This indicates that both benzene molecules are strongly bonded and probably have been completely integrated into the cluster ion.

**3.2.  $C_{18}H_x^+$ ,  $x = 4-12$ , Cluster Ion.** The results presented in the previous section suggest that the carbon skeleton of coronene **1** is preserved in the  $C_{24}H_x^+$  ions all the way down to the pure carbon cluster ion  $C_{24}^{*+}$ . Convincing arguments in favor of this assumption can be obtained by showing that  $C_nH_x^+$  ions generated by  $H\cdot$  loss from isomeric PAH ions retain their individual reactivity throughout each series of isomeric ions. Therefore,  $C_{18}H_x^+$  cluster ions from the four isomers of  $C_{18}H_{12}$ , triphenylene **2**, chrysene **3**, 1,2-benzanthracene **4**, and 2,3-benzanthracene **5** (Scheme 1), were produced by SORI-CID and

## Scheme 4

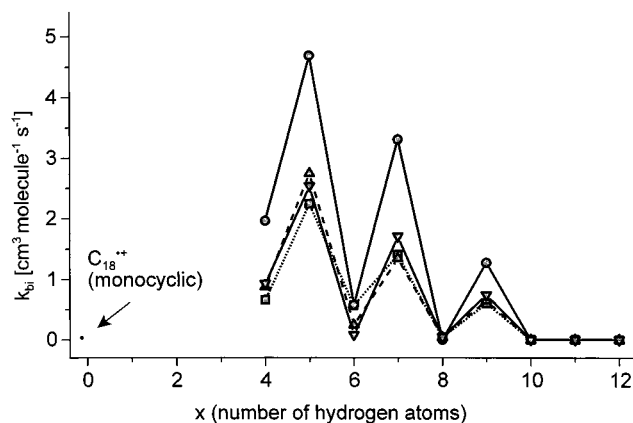
**Table 3.** Bimolecular Rate Constants,  $k_{bi}$ , of  $C_{18}H_x^+$  from Four PAH  $C_{18}H_{12}$  Isomers 2–5 with Benzene

cluster ion	$k_{bi}^{a,c}$				$k_{ADO}^{a,b}$
	triphenylen 2	chrysene 3	1,2-benzanthracene 4	2,3-benzanthracene 5	
$C_{18}H_{12}^{*+}$	no reaction	no reaction	no reaction	no reaction	987
$C_{18}H_{11}^{*+}$	no reaction	no reaction	no reaction	no reaction	988
$C_{18}H_{10}^{*+}$	no reaction	no reaction	no reaction	no reaction	988
$C_{18}H_9^+$	0.60 (47)	1.27 (100)	0.65 (51)	0.74 (58)	989
$C_{18}H_8^{*+}$	0.04 (80)	no reaction	0.04 (80)	0.05 (100)	989
$C_{18}H_7^+$	1.40 (42)	3.00 (100)	1.34 (41)	1.70 (57)	990
$C_{18}H_6^{*+}$	0.57 (98)	0.58 (100)	0.25 (43)	0.08 (14)	990
$C_{18}H_5^+$	2.24 (48)	4.68 (100)	2.74 (59)	2.53 (54)	991
$C_{18}H_4^{*+}$	0.66 (34)	1.96 (100)	0.88 (45)	0.93 (47)	991

<sup>a</sup>  $\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup> The  $k_{ADO}$  is calculated by the method of ref 39. <sup>c</sup> The numbers (in %) in parentheses are relative  $k_{bi}$  values to the highest one in each of the  $C_{18}H_x^+$  isomers.

reacted with benzene using the procedures described before. Unfortunately, in the case of  $C_{18}H_{12}$ , the successive elimination of H<sup>•</sup> atoms by SORI-CID terminates always at  $C_{18}H_4^{*+}$ . Further elimination of H<sup>•</sup> atoms was difficult because a fragmentation of the carbon skeleton cannot be avoided,<sup>30</sup> which resulted in  $C_{18}H_x^+$  intensities too small for kinetic measurements.

**Rate Constants of  $C_{18}H_x^+$ ,  $x = 4-12$ .** The ion/molecule reactions of the four series of  $C_{18}H_x^+$  ions,  $x = 4-12$ , from 2–5 with benzene show again a bimodal behavior due to the presence of a fraction of none or only slowly reacting ions especially in the case of the  $C_{18}H_{2m}^{*+}$  cluster radical cations containing an even number of H<sup>•</sup> atoms, in close analogy to the  $C_{24}H_{2m}^{*+}$  ions. The decay of the reactive components again agreed always with pseudo-first-order kinetics, and Table 3 summarizes the  $k_{bi}$  for the reactions of  $C_{18}H_x^+$  ions from 2–5 with benzene, derived in the usual way from the pseudo-first-order rate constants  $k_{exp}$ , together with the product ions and the branching ratios. All rate constants  $k_{bi}$  are much lower than the theoretical collisional rate constants  $k_{ADO}$ . This indicates also that the ion/molecule reactions of  $C_{18}H_x^+$  with benzene are controlled by a chemical activation barrier along the reaction coordinate. The rate constants for the reactions of the  $C_{18}H_{12}^{*+}$ ,  $C_{18}H_{11}^{*+}$ , and  $C_{18}H_{10}^{*+}$  ions from all four isomeric PAHs are below the limit of measurability. Figure 3 shows a plot of the rate constants  $k_{bi}$  against the number of H<sup>•</sup> atoms in the cluster ion for each series of  $C_{18}H_x^+$  ions. The odd/even modulation of the reactivity for the  $C_{18}H_x^+$  ions derived from a certain isomer is in accord with the reactivity pattern of  $C_{24}H_x^+$  ions described above, but the variation of  $k_{bi}$  between the  $C_{18}H_x^+$  ions with the odd and even number of H<sup>•</sup> atoms is much more accentuated. It is very noticeable that the reactivities of the  $C_{18}H_x^+$  ions with a certain  $x$  from the 4  $C_{18}H_{12}$  isomers are positively different outside the estimated experimental error, that the even-electron  $C_{18}H_{2m}^{*+}$  ions exhibit more pronounced differences, and that the differences become larger with a decrease in the number of the H<sup>•</sup>

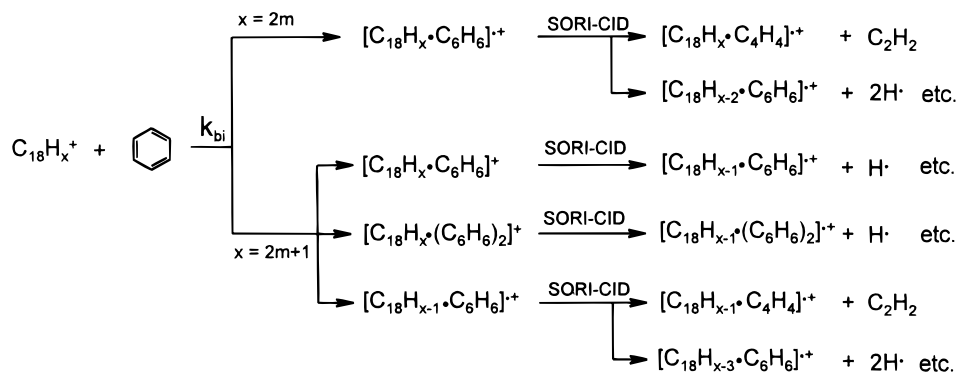


**Figure 3.** Variation of the rate constant  $k_{bi}$  of the reaction of  $C_{18}H_x^+$  cluster ions and benzene with the number  $x$  of hydrogen atoms. (■,  $C_{18}H_x^+$  derived from 2; ●,  $C_{18}H_x^+$  derived from 3; ▲,  $C_{18}H_x^+$  derived from 4; ▼,  $C_{18}H_x^+$  derived from 5).

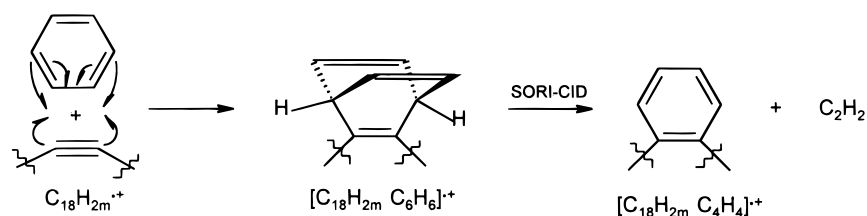
atoms. For the ions of  $C_{18}H_9^+$ ,  $C_{18}H_7^+$ , and  $C_{18}H_4^{*+}$ , the order of the reactivities from the isomers is chrysene 3 > 2,3-benzanthracene 5 > triphenylene 2 and 1,2-benzanthracene 4. However, for the other ions this order is changed with the exception of a higher reactivity of  $C_{18}H_x^+$  generated from chrysene 3. All these results indicate that the reactivity of  $C_{18}H_x^+$  is highly dependent on the structure of the parent PAH. It is reasonable to conclude that the  $C_{18}H_x^+$  ions resulting from the low-energy excitation of the SORI-CID retain the original skeleton of the parent PAHs.

**Structure of Product Ions.** Analogous to the reactions of  $C_{24}H_x^+$  from 1 with benzene, the odd/even alternation of the two reaction channels, i.e., addition of benzene and addition followed by elimination of H<sup>•</sup>, is observed also for the 4 series of  $C_{18}H_x^+$  ions generated from 2–5. The main product ions are  $[C_{18}H_x \cdot C_6H_6]^{*+}$  and  $[C_{18}H_x \cdot (C_6H_6)_2]^{*+}$  for the reactions of the

## Scheme 5



## Scheme 6



**Table 4.** Products of the Reactions of  $C_{18}H_x^+$ ,  $x = 4-9$ , from Triphenylene **2**, with  $C_6H_6$  and Their Fragments of SORI-CID

cluster ion	product ions	branching ratio (%) <sup>a</sup>	fragments of SORI-CID	
			ion + neutrals <sup>b</sup>	rel int (%) <sup>c</sup>
$C_{18}H_9^+$	$[C_{18}H_9·C_6H_6]^+$	66	$[C_{18}H_8·C_6H_6]^+ + H·$	42
			$[C_{18}H_7·C_6H_6]^+ + 2H·$	16
			$[C_{18}H_6·C_6H_6]^+ + 3H·$	36
			$[C_{18}H_8·C_4H_4]^+ + H, C_2H_2$	6
$C_{18}H_8^{*+}$	$[C_{18}H_8·C_6H_6]^{*+}$	26	$[C_{18}H_7·C_6H_6]^+ + H·$	18
			$[C_{18}H_6·C_6H_6]^+ + 2H·$	82
			$[C_{18}H_6·C_6H_6]^{*+} + H·$	100
$C_{18}H_7^+$	$[C_{18}H_7·C_6H_6]^+$ $[C_{18}H_7·(C_6H_6)_2]^{*+}$ $[C_{18}H_6·C_6H_6]^{*+}$	46	$[C_{18}H_5·C_6H_6]^+ + H·$	26
			$[C_{18}H_4·C_6H_6]^{*+} + 2H·$	45
			$[C_{18}H_6·C_4H_4]^+ + C_2H_2$	29
			$[C_{18}H_5·C_6H_6]^+ + H·$	22
$C_{18}H_6^{*+}$	$[C_{18}H_6·C_6H_6]^{*+}$	27	$[C_{18}H_4·C_6H_6]^{*+} + 2H·$	57
			$[C_{18}H_6·C_4H_4]^+ + C_2H_2$	21
			$[C_{18}H_4·C_6H_6]^{*+} + H·$	100
			$[C_{18}H_3·(C_6H_6)_2]^{*+} + 2H·$	17
$C_{18}H_5^+$	$[C_{18}H_5·C_6H_6]^+$ $[C_{18}H_5·(C_6H_6)_2]^{*+}$	39	$[C_{18}H_2·(C_6H_6)_2]^{*+} + 3H·$	23
			$[C_{18}H_2·C_6H_6]^{*+} + 2H·$	100
			$[C_{18}H_4·C_6H_6]^{*+}$	20
			$[C_{18}H_3·C_6H_6]^+ + H·$	11
$C_{18}H_4^{*+}$	$[C_{18}H_4·C_6H_6]^{*+}$	65	$[C_{18}H_2·C_6H_6]^{*+} + 2H·$	44
			$[C_{18}H_4·C_4H_4]^+ + C_2H_2$	45
			$[C_{18}H_3·C_6H_6]^+ + H·$	11

<sup>a</sup> —cSee the footnotes for Table 2.

$C_{18}H_{2m}^{*+}$  radical cations, and  $[C_{18}H_{2m+1}·C_6H_6]^+$  and  $[C_{18}H_{2m}·C_6H_6]^{*+}$  for that of the  $C_{18}H_{2m+1}^+$  cations. Reactions with benzene-*d*<sub>6</sub> also prove that in these cases the  $H·$  atom lost stems from the  $C_{18}H_x^+$  moiety and not from the added benzene molecule.

Isomeric  $C_{18}H_x^+$  ions may give product ions of different structures by their reactions with benzene. Therefore, the product ions from the reactions of the  $C_{18}H_x^+$  ions with benzene have been analyzed using the SORI-CID method. As an example, the SORI-CID fragments of the  $C_{18}H_x^+$  product ions of triphenylene **2** are summarized in Table 4. Identical CID behavior is observed in all 4 series of ions. The primary  $[C_{18}H_{2m+1}·C_6H_6]^+$  product ions fragment predominantly or exclusively by loss of one  $H·$  atom, but the primary  $[C_{18}H_{2m}·C_6H_6]^{*+}$  radical cation products dissociate by two different

pathways. The first one is loss of one or several  $H·$  atoms, and the loss of 2  $H·$  (or  $H_2$ ) is usually favored. The second one is loss of acetylene  $C_2H_2$  as illustrated in Scheme 5. By studying the product ions of  $C_{18}H_x^+$  with benzene-*d*<sub>6</sub> it is demonstrated that this  $C_2H_2$  comes exclusively from the  $C_6H_6$  moiety of the ions, in contrast to the loss of  $H·$  (or  $nH·$ ) which involves only that part of the product ion arising from the original  $C_{18}H_x^+$  cluster ion. These results are strong evidence that at least the  $C_{18}H_{2m}^+$  cluster ions undergo a cycloaddition with benzene to give [2+4] addition adducts  $[C_{18}H_x·C_6H_6]^{*+}$  (Scheme 6). It is known that arynes are good dienophiles toward benzene,<sup>43</sup> and this is also to be expected for the "aryne bonds" within the  $C_nH_x^+$  ions, both the radical cation  $C_nH_{2m}^{*+}$  and the cation type  $C_nH_{2m+1}^+$ . The cycloaddition reaction of  $C_nH_x^+$  with benzene is probably slow, because a larger reaction efficiency is only observed for ions of small  $x$ . Further, the reaction is not necessarily a concerted one and may also occur via multiple steps, i.e., addition of  $C_6H_6$  to form reversibly a reaction complex and in the second step forming a stable [2+4] cycloaddition adduct. The preferred loss of one  $H·$  atom in the reactions of  $C_nH_{2m+1}^+$  with benzene might happen during this latter step. This is suggested by the practically identical behavior of the two ions  $[C_{18}H_6·C_6H_6]^{*+}$  generated by the reactions of  $C_{18}H_6^{*+}$  and  $C_{18}H_7^+$ , respectively, shown in Table 4 and Scheme 5. It remains unclear, however, why the loss of  $C_2H_2$  is not observed by SORI-CID of the product ions of the reaction of  $C_{24}H_x^+$  with benzene. Otherwise, the  $C_{24}H_x^+$  ions generated from coronene **1** and the  $C_{18}H_x^+$  ions generated from the isomeric PAHs **2-5** behave parallel in their reaction with benzene and in the properties of the reaction product ions. Of particular importance is the observation that the rate constants  $k_{bi}$  of the reaction with benzene for the cluster ions  $C_{18}H_x^+$  depend clearly on the structure of the parent PAHs down to the lowest number  $x = 4$  of  $H·$  atoms present in the ions. This supports strongly the idea that these ions retain the isomeric carbon skeleton of the parent PAHs during repeated losses of  $H·$  atoms from the rim of the ionized PAHs by SORI-CID. It can be expected safely that  $C_{24}H_x^+$  ions derived from coronene

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**1** exhibit an analogous behavior. Then, this can be extrapolated with some confidence also to the formation of  $C_{24}^{*+}$  carbon cluster ions which accordingly exist in a graphitic structure if prepared by the SORI-CID technique.

#### 4. Conclusion

Recent theoretical calculations of possible structures and their stabilities of carbon clusters containing 20,<sup>44</sup> 24,<sup>45</sup> and 28<sup>46</sup> C atoms at high levels of theory suggest that graphitic structures or even spherical fullerene structures are stable and may be even more stable than a monocyclic structure for carbon cluster ions of this size. A first and clear result from our study of the generation of carbon cluster ions  $C_{24}^{*+}$  by SORI-CID from coronene **1** and the reaction of these ions with benzene is the fact that the method used produces a  $C_{24}^{*+}$  carbon cluster ion orders of magnitude more reactive than the monocyclic  $C_{24}^{*+}$  produced by laser evaporation of graphite. Only a very small fraction of the  $C_{24}^{*+}$  ions from the SORI-CID experiment exhibit the low reactivity toward benzene attributed to the monocyclic species. A priori the high reactivity observed could be attributed to any other structure of  $C_{24}^{*+}$  besides a monocycle, but from the structures discussed in the literature<sup>45</sup> our study gives very convincing evidence that  $C_{24}^{*+}$  carbon cluster ions of a graphitic structure are formed. This is not only in accord with the high reactivity expected for this structure but is strongly corroborated by the observation that the SORI-CID method clearly gives isomeric  $C_{18}H_x^+$  cluster ions of even quite low  $H^\bullet$  content depending on the structures of the parent PAHs. A straightforward explanation of all these observations is conservation of the graphitic structure of the relevant precursor PAH. We have pointed out before<sup>29</sup> that the discussion of “dangling bonds” for graphitic carbon clusters induced an incorrect picture. It is known that 1,2-didehydrobenzene with an “aryne” triple bond is stabilized by more than 130 kJ/mol compared with the corresponding 1,2-diradical with its dangling bonds.<sup>47</sup> A similar stabilization per aryne bonds is expected for dodecadehydro-coronene  $C_{24}$  with its six aryne bonds. Therefore, this graphitic  $C_{24}^{*+}$  is better described by a structure with triple C–C bonds that are strained by bending, similar to the C–C bonds in the monocyclic  $C_{24}^{*+}$ . This may be one reason that both structures are nearly isoenergetic<sup>45</sup> isomers. Further, the intact aromaticity of the graphitic  $C_nH_x^+$  ions within the molecular plane keeps the carbon skeletons stable during the  $H^\bullet$  atom eliminating processes for both  $C_{24}H_x^+$  and  $C_{18}H_x^+$ . However, the electronic configuration of both structures differs strongly by only one delocalized  $\pi$ -electron system in the graphitic structure and two perpendicular  $\pi$ -electron systems in the monocyclic cluster ion. Therefore, very different reactivities are expected for the two isomers, and the isolated aryne “triple” C–C bonds of the graphitic cluster may contribute to the high reactivity and the characteristic reaction pathways.

The observation of stable carbon cluster ions of high reactivity which are not found among the cluster ion structures generated by laser evaporation of graphite or other methods using high energy and high temperature techniques has two interesting consequences. The first one refers to the mechanism of fullerene

growth. The current theory of fullerene formation has its basis on the stability and reactivity of intermediate monocyclic carbon cluster or carbon cluster ions which coalesce, probably by cycloaddition reactions, into large bi- and polycyclic structures which eventually yield the fullerenes as the most stable form of carbon clusters. However, the abundances of monocyclic carbon clusters in the range around 20 C atoms observed by laser evaporation are quite small. In view of our observation of carbon cluster ions of much higher reactivity it is possible that in fact these reactive carbon cluster ions of graphitic structure are the precursors of fullerenes, and that the monocyclic clusters are only the nearly unreactive “riffraff” left at the end of the reaction after depletion of this range of carbon clusters by fullerene formation. This agrees with a mechanism of generation of fullerenes in sooting flames suggested by Homann et al.<sup>48</sup> The second point of interest is that our results indicate the possibility of producing carbon cluster ions with “tailored” structures by SORI-CID of suitable precursors. In choosing such precursors it has to be considered that a multistep but low-energy route to the ionized cluster must exist. The elimination of chloro or bromo substituents from the rim of a polycyclic carbon molecule would be much better than repeated losses of  $H^\bullet$ . However, the poly- or perhalogenated compounds are difficult to prepare in pure form and usually exhibit a high melting point and a very low vapor pressure. Thus, we found them difficult to handle in an FT-ICR instrument, and it may be worthwhile to search for better precursor molecules.

While the high reactivity of the  $C_nH_x^+$  prepared in this work toward benzene especially at low  $H^\bullet$  atom content is obvious, the mechanism(s) of this reaction is not clear. All  $C_nH_x^+$  ions either react with benzene to form adducts with a benzene molecule and/or react by an addition–elimination sequence consisting of addition of a benzene molecule followed by loss of one  $H^\bullet$  atom. It is verified that the benzene molecule is bonded to the  $C_nH_x^+$  ions by formation of new C–C bonds rather than by electrostatic association because no  $C_6H_6$  losses were observed in the SORI-CID spectra of product ions. However, the groups of atoms derived from benzene and from the carbon cluster ions must remain separated entities in the product ions. This is different from the behavior of adducts of benzene<sup>18</sup> or naphthalene<sup>13</sup> to monocyclic carbon cluster ions. In these latter cases the CID spectra indicate a complete amalgamation of the original structures of the reactants, while in the present case the reaction products with benzene- $d_6$  exhibit only losses of  $H^\bullet$  atoms from the  $C_nH_x$  moiety and/or losses of  $C_2D_2$  exclusively from the benzene- $d_6$  moiety. The latter decomposition indicates that one of the reactions of the  $C_nH_x^+$  ions with benzene corresponds to a cycloaddition, in which the graphitic  $C_nH_x^+$  ions exhibit a benzyne reactivity and act as a dienophile toward benzene in a Diels–Adler reaction. The structure of this primary adduct  $[C_nH_x \cdot C_6H_6]^+$  is suggested to be a graphitic plate with a 1,4-bridged benzene at the rim as shown in Scheme 6. This bridge is eliminated during CID. However, it is not clear why this cycloaddition is only observed for the smaller graphitic  $C_{18}H_x^+$  carbon cluster ions and not for  $C_{24}H_x^+$ . Another possible mechanism to attach a benzene molecule to a  $C_nH_x^+$  cluster ion is electrophilic attack of the carbonium ion center of  $C_nH_{2m+1}^+$  cations or electrophilic as well as radical attack of the radical site of the  $C_nH_{2m}^{*+}$  radical cations on benzene followed by migration of the proton from the  $\sigma$ -complex to the polycyclic system of the graphitic part of

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the product ion. This reaction may be expected to be favored over the cycloaddition for even-electron cluster cations and for odd-electron cluster radical cations containing no aryne bond but two separate local reaction centers for the positive charge and the radical. It is possible that the products of this addition mechanism lose a H• atom by CID. Thus, the observation of a different behavior of the product ions of the reaction of  $C_nH_x^+$  ions with benzene on CID can be taken as evidence that isomeric graphitic cluster ions with respect to the position of the positive charge and the radical electron are formed by the losses of H• atoms from an ionized PAH by SORI-CID and that several parallel mechanisms operate in the reaction of these ions with

benzene. This has been studied further by other ion/molecule reactions of the  $C_nH_x^+$  cluster ions.

**Acknowledgment.** The assistance of Dr. H. Sievers and Dipl. Ing. M. Terrey during the FT-ICR measurements is gratefully acknowledged. The FT-ICR instrument used in this work is a grant by the Deutsche Forschungsgemeinschaft, and we gratefully acknowledge additional financial assistance by the Fonds der Chemischen Industrie. X.G. thanks the Alexander-v.-Humboldt-Stiftung (Bonn, Germany) for a research stipendium during his stay at the Universität Bielefeld.

JA984275E