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Reactivity and Structure of Hydrogenated Carbon Cluster Ions $C_nH_x^+$ ($n = 18, 20, 24$; $x = 4-12$) Derived from Polycyclic Aromatic Hydrocarbons by Splitting off $H^\bullet$ Atoms: Reactions with Dimethyl Disulfide

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The ion/molecule reactions of hydrogenated carbon cluster ions C_nH_x+, $n = 18, 20, 24$; $x = 4-12$, in the gas phase with CH_3SSCH_3 (DMDS) were investigated using Fourier transform ion cyclotron resonance (FT-ICR) spectrometry. The cluster ions $C_{18}H_x^+$ were prepared from the four $C_{18}H_{12}$ isomers chrysene (**1**), 1,2-benzanthracene (**2**), triphenylene (**3**), and naphthacene (**4**); cluster ions $C_{20}H_x^+$ from perylene (**5**), $C_{20}H_{12}$; and cluster ions $C_{24}H_x^+$ from coronene (**6**), $C_{24}H_{12,}$ by consecutive elimination of $H^\bullet$ atoms using the "soft" activation technique of the sustained off-resonance irradiation collision-induced dissociation (SORI−CID) available on FT-ICR. The products, bimolecular rate constants k_{bi}, reaction channels and their branching ratios, and SORI−CID fragments of the product ions of the ion/molecule reactions with DMDS provide valuable information about the reactivity and structure of the cluster ions $C_nH_x^+$. First, it is shown for cluster ions $C_{18}H_x^+$ that the rate constants of the reaction with DMDS of the individual species depend clearly on the structure of the parent polycyclic aromatic hydrocarbon (PAH) of the ions, even for clusters of low hydrogen content. Obviously, the cluster ions remember the skeleton of the parent PAH and, therefore, differ in structure from those formed by laser evaporation of graphite reported by Bowers and co-workers. Second, the bimolecular rate constants increase with decreasing number of hydrogen atoms present and alternate regularly in all series of cluster ions $C_nH_x^+$ with odd and even number x of hydrogen atoms. These effects parallel the results obtained earlier for the ion/molecule reaction of $C_nH_x^+$ with benzene and confirm a general reactivity scheme of these cluster ions. Third, two kinds of the reactivity of the cluster ions $C_nH_x^+$ with DMDS are observed, i.e., a carbonium-like (*C^+ reactivity*) and an strained aryne-bond-like reactivity (*aryne reactivity*). Both reactivities display characteristic reaction products with DMDS and can be related to the presence of reaction centers in the cluster ions corresponding to an aryl ion carbenium center, a σ-aryl radical center, and a strained triple bond of an (ionized) aryne. These reactions centers are expected to arise from losses of H atoms from the parent PAH if the polycyclic carbon skeleton survives the fragmentation, as previously suggested from the results of a reaction of the hydrogenated carbon cluster ions with benzene.

Introduction

Several studies of the reactions and the structures of ionized small carbon clusters $C_n^{\bullet+}$ with $n \leq 24$ as well as of partially hydrogenated species $C_nH_x^+$ ($x \leq 5$) have been reported during the past decades.[1−3] Both species are considered to play an important role in astrochemistry[4] and combustion[5] processes and in the formation of hollow-cage fullerenes.[6] The structures of $C_n^{\bullet+}$ ($n \leq 24$) were studied by Bowers[2,7] and by Jarrold et al.[8] using ion chromatography (IC),[9] and with increasing number of C atoms the ion $C_n^{\bullet+}$ were reported to be linear chains, monocyclic rings, and bicyclic rings. From $C_{11}^{\bullet+}$ to $C_{27}^{\bullet+}$, the monocyclic rings are highly predominant, but for larger carbon cluster ions other structures compete. Besides the structures mentioned above, planar graphitic carbon clusters were observed to appear at about $C_{29}^{\bullet+}$ to $C_{60}^{\bullet+}$, [2,7a−c,10] while any curved graphitic structures were reported to be absent. Interestingly, graphitic structures were predicted by theoretical calculations to be stable, starting already from $C_{20}^{\bullet+}$, and were expected to compete in stability with monocyclic structures at this size range.[11] Therefore, graphitic $C_n^{\bullet+}$ should be considered also as precursors[6] for the formation of fullerenes, even though the experimental results[2,7,8,12] show dominant monocyclic structures in the case of smaller clusters.

It is suspicious that in most experimental studies the carbon cluster ions were generated by laser evaporation of graphite, with exception of the electron impact induced dechlorination of perchlorinated polycyclic aromatic hydrocarbons (PAH).[13] Studies of structures and reactivities[13,14] indicated that identical monocyclic clusters $C_n^{\bullet+}$ are generated by both methods. This is very likely due to the high energy needed both for laser evaporation and for electron impact induced dechlorination to prepare these cluster ions. A careful study[15] of cluster ions $C_{12}^{\bullet+}$ derived from decachloroacenaphthene $C_{12}Cl_{10}^{\bullet+}$ failed to observe any $C_{12}^{\bullet+}$ keeping the skeleton of this PAH, although the PAH structure was conserved in some ions $C_{12}Cl_x^{\bullet+}$ formed by the loss of only a few Cl atoms. Nonetheless, a previous study[16] has shown that graphitic $C_{24}^{\bullet+}$ might have been formed indeed from perchlorocoronene, $C_{24}Cl_{12}$, as a coexisting isomer using the more gentle technique of multiple-excitation collisional activation (MECA) and Fourier transform ion−cyclotron resonance (FT-ICR) spectrometry to remove the 12 Cl atoms from the precursor.

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In our preceding study[17] on the generation of $C_n^{\bullet+}$ and $C_nH_x^+$, we have used the sustained off-resonance irradiation and collision-induced dissociation (SORI−CID) technique[18] available in FT-ICR spectrometry as a new approach to prepare these cluster ions in the gas phase. Using SORI−CID the stepwise elimination of H atoms from the molecular ions of a PAH was possible by isolating the product ion of each fragmentation step. This procedure avoids the accumulation of more excess energy in the ions than necessary to initiate the fragmentation of lowest activation energy, and in the case of PAH and $C_nH_x^+$ ions derived therefrom, this is usually the loss of one H atom. As a result, cluster ions $C_nH_x^+$, $n = 13-24$ and $x = 1-11$ and in certain cases the "pure carbon cluster ion" $C_n^{\bullet+}$ as well were formed with sufficient abundance for further studies. Studies of the ion/molecule reactions[19] of benzene with the series of cluster ions $C_nH_x^+$, $n = 18$ and 24, indicated that the skeleton of the parent PAH was very likely retained by the ions $C_nH_x^+$. This is of interest in connection with a recent report by Bowers and co-workers[3] on the structures of $C_nH_x^+$, $n \leq 22$ and $x \leq 5$, formed by adding H_2 to the plasma during laser evaporation of graphite.[20] By this technique, monocyclic species were found again predominantly. However, new isomeric components of $C_nH_x^+$, $n \geq 15$ and $x = 4, 5$, were observed and were considered as species related to the PAH formation. Their structures were assigned to be a benzene ring with a carbon loop attached at ortho positions, but no species with polycyclic PAH skeletons were considered. Further, in a previous study[19] we prepared by SORI−CID an ion, $C_{24}^{\bullet+}$, which exhibits significantly higher reactivity than that of monocyclic $C_{24}^{\bullet+}$,[14] and this reactive $C_{24}^{\bullet+}$ was assigned a graphitic carbon cluster ion. From these studies it emerges that the structure of a carbon cluster ion in the gas phase depends more on the mode of preparation that assumed previously, and that also rather small carbon cluster ions can employ a broad variety of stable structures. Therefore, it is worthwhile to characterize the species $C_nH_x^+$ created from PAH by the "soft" SORI−CID method by additional ion/molecule reactions. A reagent which has proven useful to characterize the structure of gaseous ions, in particular distonic radical cations, is dimethyl disulfide (CH_3SSCH_3; DMDS).[21] In this paper, we report a study of the ion/molecule reactions of DMDS with four series of the cluster ions $C_nH_x^+$, $n = 18$, $x = 4-10$, and of some ions $C_nH_x^+$, $n = 20$ and 24, which were derived from suitable PAH by the SORI−CID method. The results indicate that the ions $C_nH_x^+$ display similar differences of their reactivity toward DMDS than observed in the reaction with benzene, but that ion/molecule reactions with DMDS can serve as better probes to the structures of cluster ions $C_nH_x^+$.

Experimental Section

All compounds used in this study are commercially available as pure substances and used without further purification.

All FT-ICR experiments were carried out on a Bruker CMS 47X FT-ICR spectrometer equipped with a 4.7 T superconducting magnet, an Infinity Cell[22]and an external electron ionization (EI) source.[23] The cluster ion generation and the ion/molecule reactions were studied as described before.[17,19] Briefly, the molecular ions of the PAH were generated in the external source by the 30 eV EI. All ions formed in the ion source were transferred into the FT-ICR cell, and the molecular ions were isolated using the standard procedures of ejection of all unwanted ions by a broad band radio frequency (rf) pulse and a series of single rf pulses of appropriate frequencies. Then, the first step of the SORI−CID[18] was applied to these ions by setting an "off-resonance" irradiation pulse, where the frequency was 150−380 Hz aside from the natural cyclotron frequencies of the selected ions. The excitation potential V_{p-p} was about 0.5−0.9 V. A pulse of argon was admitted into the cell as the target gas for the collision activation at a peak pressure estimated to be about 10^{-5} mbar. With this procedure, ions $C_nH_{11}^+$ were produced efficiently. By applying again similar SORI−CID to the product ion $C_nH_{11}^+$, secondary ions $C_nH_{10}^{\bullet+}$ were generated, and so on. After a suitable series of SORI−CID experiments, the target cluster ions $C_nH_x^+$ were isolated by the same procedure described above. Special care was taken for optimizing the parameters of SORI−CID to minimize the ion loss and to avoid any excitation of the product ions $C_nH_x^+$. Generally, at least in our experimental conditions, the ions $C_nH_x^+$ formed by SORI−CID are already kinetically "cool" after isolation. However, for removing any unintended excitation from the selected ions $C_nH_x^+$, a pulsed valve was opened for 15 ms to allow a pressure of argon (peak pressure ca. 10^{-5} mbar) to enter the FT-ICR cell and thermalize the ions $C_nH_x^+$ for 1−2 s. This was followed by ejections using single rf pulses of selected frequencies to remove any reaction product ions formed during this period.

For executing ion/molecule reactions, a variable delay time (0−80 s) was used to permit the individual cluster ions $C_nH_x^+$ to react with DMDS as a neutral reactant present in the FT-ICR cell at a constant background pressure of $(1-12) \times 10^{-8}$ mbar and at 300 K. The experimental pseudo-first-order rate constants k_{exp} of the ion/molecule reactions were determined by observing the decay of the intensity of the ions $C_nH_x^+$ as a function of the reaction time ("kinetic plot"), and by fitting the intensity curves with the appropriate kinetic expression using the Origin program.[24] The bimolecular rate constants k_{bi} were calculated by taking into account the number density of the neutral reactant in the FT-ICR cell derived from its partial pressure. The rate constants k_{exp} reported are very well reproducible ($< \pm 10\%$), but are estimated to be accurate only within 30% because the main error is due to the measurement of the partial pressure of the neutral reactants. The reaction efficiency (eff. %) was obtained from the ratio of the experimental k_{bi} and the theoretical collision rate constant k_{col}.[25] The pressure within the FT-ICR cell was calibrated by rate measurements of the reactions $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^+ + {}^{\bullet}CH_3$ ($k_{bi} = 1.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} [26]) and $NH_3^{\bullet+} + NH_3 \rightarrow NH_4+ + {}^{\bullet}NH_2$ ($k_{bi} = 2.2 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} [27]) and corrected by the sensitivity constant of the reactant with standard methods.[28]

SORI−CID of some product ions of the ion/molecule reactions was accomplished as described in a previous paper.[19] The soft excitation of SORI−CID makes it possible to observe mainly the dissociation pathway of lowest energy, thus providing more structure information for this study, and its high dissociation efficiency enables to study also some product ions of low intensity.

Results and Discussion

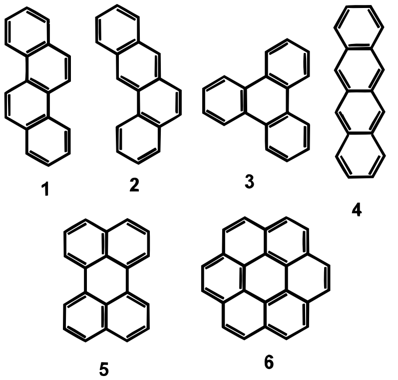
SORI−CID is a modern method of collisional activation,[18] which excites the ions by slight off-resonance irradiation, and which induces under the experimental condition used in this work the fragmentation of lowest activation energy[29] of mass-selected ions. Despite the fact that dissociation of the carbon frames of the molecule ions of PAHs is observed at the high activation energy of conventional CID,[29] elimination of a single H atom (or $2H^{\bullet}/H_2$ in some cases) has been proven to be the most favorable process during SORI−CID,[17] and, evidently, the resulting cluster ions $C_nH_x^+$ remember the carbon skeleton of

TABLE 1: Bimolecular Rate Constants, k_{bi}, and Reaction Efficiency, eff [%], of the Reaction of Hydrogenated Carbon Cluster Ions $C_nH_x^+$ with DMDS

	1 ($n = 18$)		2 ($n = 18$)		3 ($n = 18$)		4 ($n = 18$)		5 ($n = 20$)		6 ($n = 24$)	
cluster ion	k_{bi}[a]	eff[b]	k_{bi}[a]	eff[b]	k_{bi}[a]	eff[b]	k_{bi}[a]	eff[b]	k_{bi}[a]	eff[b]	k_{bi}[a]	eff[b]
C_nH_{12}	n.r.[d]		n.r.[d]		n.r.[d]		n.r.[d]		n.r.[d]		n.r.[d]	
C_nH_{11}	n.r.[d]		n.r.[d]		n.r.[d]		n.r.[d]		n.r.[d]		3.06	23
C_nH_{10}	n.r.[d]		n.r.[d]		n.r.d)		n.r.[d]		n.r.[d]		3.50	27
C_nH_9 [c]	8.80	67	1.95	15	9.40	71	3.11	24	6.67	51	4.76	36
C_nH_8 [c]	3.37	26	0.68	5	6.28	48	0.79	6	2.80	22	4.31	33
C_nH_7	4.71	36	3.26	25	10.6	81	4.59	35	9.53	73		
C_nH_6	5.24	40	3.11	24	8.04	61	4.46	34	8.02	62		
C_nH_5	9.93	75	8.21	62	12.6	96	9.10	69	12.3	95		
C_nH_4	9.16	69	6.56	50	8.90	67	6.34	48	13.6	104		

[a] Data $\times 10^{-10}$ [$cm^3\ s^{-1}$ molecule^{-1}]. [b] $k_c = 13.2 \times 10^{-10}$ [$cm^3\ s^{-1}$ molecule^{-1}]. [c] Bimodal decay; k_{bi} mean value for reactive ions. [d] Entry n.r. denotes no reaction.

SCHEME 1 Structures of the PAH.



the precursor PAH[19], probably without any rearrangement of the carbon frame. In the present study, the ions $C_{18}H_x^+$, $x = 4-12$, were prepared from the four isomers of $C_{18}H_{12}$, chrysene **1,** 1,2-benzanthracene **2**, triphenylene **3**, and naphthacene **4**, the ions $C_{20}H_x^+$, $x = 4-12$ from $C_{20}H_{12}$, perylene **5**, and the ions $C_{24}H_x^+$, $x = 6-11$, from $C_{24}H_{12}$, coronene **6**, (Scheme 1) using SORI−CID.

Reactions of Ions $C_{18}H_x^+$ from Isomeric PAH with DMDS. As in the reactions with benzene,[19] a different reactivity of ions $C_{18}H_x^+$ of different origin was observed for the reactions with DMDS. Generally the reactivity of the ions $C_{18}H_x^+$ toward DMDS increases with decreasing hydrogen content, and this effect is overlaid by an alternation of the reactivity between cations (odd number of hydrogen atoms: $x = m + 1$) and radical cations (even number of hydrogen atoms: $x = m$), as observed for the reactions with benzene.[19] The differences of the bimolecular rate constants k_{bi} (Table 1; Figure 2) are especially large for isomeric ions derived from **3** on the one side and **1**, **2**, and **4** on the other side, but differences are also seen between the isomeric ions derived from the latter PAH. There are exceptions, and in some cases the rate constants k_{bi} are not significantly different. However, no systematic correlation between the four series of ions is observed. For example, the rate constants of ions $C_{18}H_9^+$ derived from **1** and **3** are almost identical, while ions $C_{18}H_8^+$ derived from **2** and **4** and ions $C_{18}H_7^+$ derived from **1** and **4** exhibit almost identical rate constants. It should be remembered that the ion $C_{18}H_x^+$ in each series of decreasing number x of hydrogen atoms is derived from the ion $C_{18}H_{x+1}^+$ of the same series as the precursor. Hence, if at a certain stage isomerization occurs between ions $C_{18}H_x^+$ of isomeric series, all of the following ions $C_{18}H_{x-1}^+$, etc., should be identical. This is clearly not the case. Therefore, the whole series of results leaves no doubt that the cluster ions $C_{18}H_x^+$ derived from isomeric parent PAH are still isomeric species, confirming the conclusion originally derived from the reaction with benzene.[19]

However, compared to the reaction with benzene, the DMDS reaction yielded a much broader spectrum of reaction products. Further, the reactions of the hydrogen-rich species ($x = 9$, 8) deviated somewhat from pseudo-first-order kinetics which are expected for ions $C_{18}H_x^+$ of a uniform structure (see, for example, Figure 1a), and a somewhat better fit of the kinetic plots was achieved by using a bimodal decay. Obviously, the SORI−CID technique creates not only isomers from isomeric PAH precursors but also isomers within each series by elimination of hydrogen atoms from different positions of the PAH. The bimolecular rate constants k_{bi} derived from the kinetic plots are listed in Table 1, and Table 2 shows the composition of the product ion mixture at the end of the reaction.[30]

No reaction was observed for the most hydrogen rich ions $C_{18}H_x^+$, $x = 10-12$. These ions are not really “cluster ions” but correspond to “normal” molecular ions $C_{18}H_{12}^{\bullet+}$ of the isomeric PAH, to their aryl cations $C_{18}H_{11}^+$, and to didehydroarene (“aryne”) radical cations $C_{18}H_{10}^{\bullet+}$. The gas-phase reactions of these stable ions with DMDS are presumably endothermic. The kinetic plots for the reaction of ions $C_{18}H_9^+$, $C_{18}H_8^{\bullet+}$, and $C_{18}H_7^+$ derived from **1** are shown as examples in Figure 1. It is obvious that only a fraction of the ions $C_{18}H_9^+$ and ions $C_{18}H_8^{\bullet+}$ react with excess DMDS while about 7% and 43%, respectively, are unreactive. An analogous behavior was observed for ions $C_{18}H_x^+$ generated from **2**, **3**, and **4**. However, for all ions $C_{18}H_x^+$ with $x \leq 7$ no fraction of unreactive ions is observed.

The observation of a fraction of unreactive ions demonstrates that obviously a mixture of isomeric ions is formed from each parent PAH by loss of three and four H atoms, respectively.[31] The formation of isomeric $C_{18}H_x^+$ from a PAH by sequential loss of a few H atoms from the molecular ions is expected, since the C−H bond dissociation energy at the different positions at the PAH rings is not significantly different. Such positional isomers are very likely also formed during the generation of ions $C_{18}H_x^+$, $x = 4-7$, from each of the PAH **1**−**4**, but in the kinetic plots of these ions the decay is described adequately by pseudo-firsr-order kinetics using only one rate constant k_{exp}. Obviously, the positional isomers $C_{18}H_x^+$, $x = 4-7$, exhibit rather similar reactivities toward DMDS. Nonetheless, the mixtures of ions $C_{18}H_x^+$ generated from the different precursor PAH display distinctly different rate constants.

In addition to the fraction of unreactive ions, a small fraction of ions $C_{18}H_x^+$ with $x \leq 9$ undergoes charge exchange with DMDS. The resulting molecular ion of DMDS reacts with excess DMDS by formation of the ion $(CH_3S)_3^+$, m/z 141, as the secondary reaction product. The ionization energy (IE) of

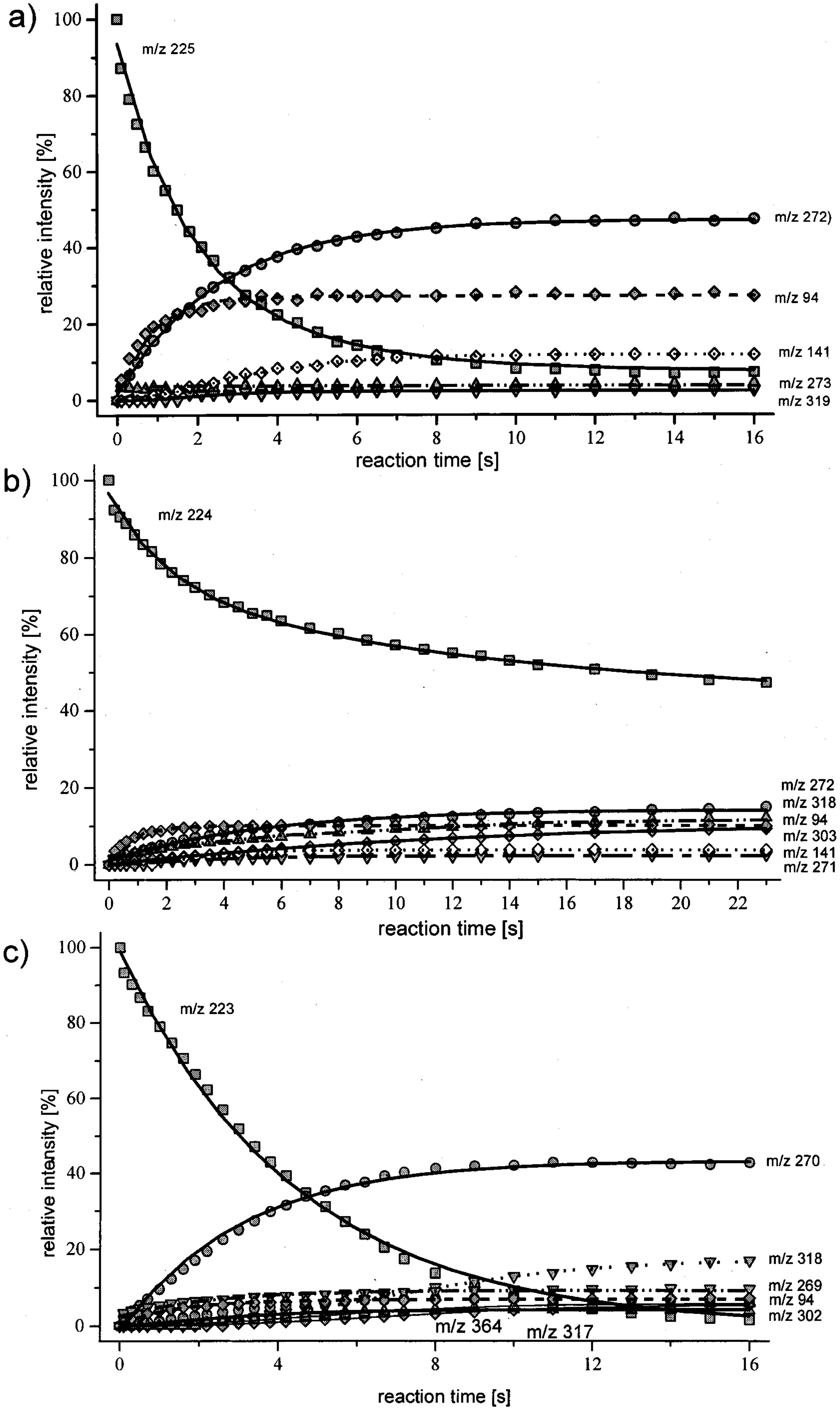


Figure 1. Kinetic plots for the reaction of cluster ions (a) $C_{18}H_9^+$, *m/z* 225, (b) $C_{18}H_8^{\cdot+}$, *m/z* 224, and (c) $C_{18}H_7^+$, *m/z* 223, derived from **1**, with DMDS.

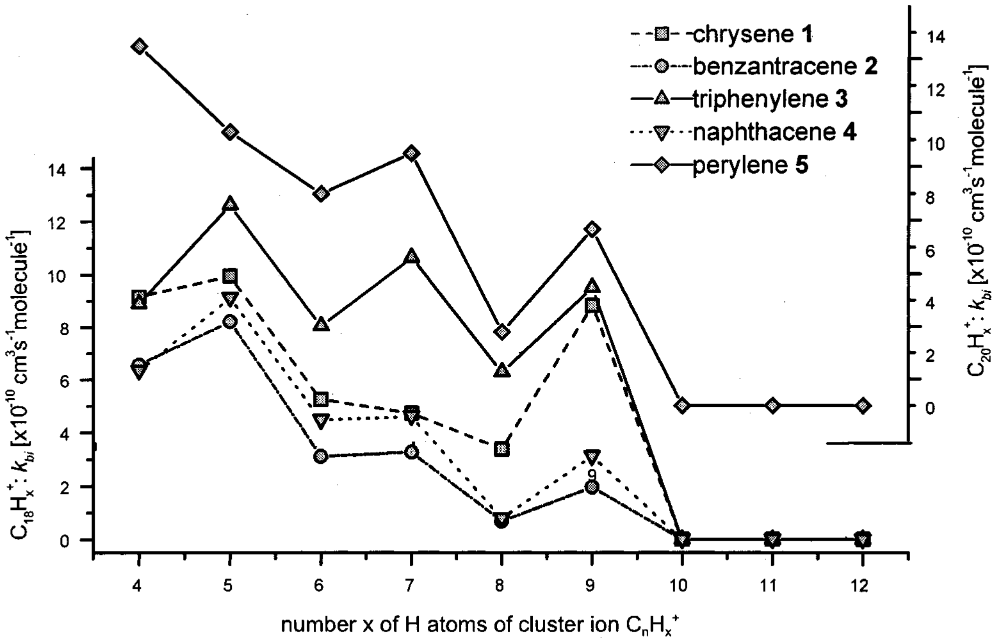


Figure 2. Dependence of the bimolecular rate constants k_{bi} of the reaction of isomeric cluster ions $C_{18}H_x^+$, derived from **1**−**4**, and cluster ions $C_{20}H_x^+$, derived from **5**, with DMDS.

SCHEME 2 Products of Primary Reactions of Cluster Ions $C_nH_x^+$ with DMDS.

$C_nH_x^+ + DMDS \longrightarrow [C_nH_x{\bullet}CH_3S]^{\bullet+}$ (x odd number: main reaction)

$\longrightarrow [C_{18}H_5{\bullet}CH_3SH]^+$ (x even number: main reaction)

$\longrightarrow [C_nH_x{\bullet}CH_3S_2]^{\bullet+}$

$\longrightarrow [C_nH_x{\bullet}(CH_3S)_2]^{\bullet+}$

DMDS of 8.18 eV[32] is higher than that of the $C_{18}H_{12}$ PAH isomers **1**−**4** (IE(chrysene) = 7.60,[33] IE(benzanthracene) = 7.45 eV,[33] IE(triphenylene) = 7.87,[33] IE(naphthacene) = 6.97 eV[33]). No charge exchange was observed for ions $C_{18}H_{12}^{\bullet+}$ or $C_{18}H_{11}^+$ generated from **1**−**4**. For the more dehydrogenated species $C_{18}H_x$, $x \leq 8$, the IEs can be expected to be higher than the IE of the parent PAH, depending on the structure of these ions.[33,34] However, charge exchange of ions $C_{18}H_x^+$ with DMDS is observed mostly during the initial period of the reaction. This could indicate either the presence of isomer(s) of especially high IE in the $C_{18}H_x^+$ mixture which undergo fast charge exchange, for example isomers containing multiple aryne-π bonds, or the presence of a fraction of "hot" ions. Because of the rather difficult experimental procedure in generating the ions $C_{18}H_x^+$ it cannot be rigorously excluded that some of the ions contain still some excess kinetic or internal energy to drive endothermic charge exchange, despite the cooling of the ions by admission of a pressure pulse of argon into the FT-ICR cell before the reaction with DMDS. Since the cluster ions may be cooled further by unreactive collisions with DMDS, this would explain fast charge exchange only during the initial period of the reaction.

Alternating Reactivity of Odd and Even Electron Cluster Ions $C_nH_x^+$ toward Dimethyl Disulfide. As already mentioned for ions $C_{18}H_x^+$, the total reactivity of all cluster ions $C_nH_x^+$, n = 18, 20, 24, with DMDS increases with the decreasing number x of H atoms of the ion, and the reactivity alternates between ions containing an odd and even number of H atoms. This is shown by the k_{bi} of the ions $C_{18}H_x$ and $C_{20}H_x^+$ in Figure 2.

In addition, the main products of the reactions of these ions with DMDS show also a systematic correlation with the odd/even number of hydrogen atoms of the cluster ions (Scheme 2). The molecular ions of the PAH are radical cations with an odd number of valence electrons but an even number of hydrogen atoms. Hence, the elimination of one H atom in each step switches the electronic nature of the resulting cluster ion in each step between an even-electron cation $C_nH_{m+1}^+$ and an odd-electron radical cation $C_nH_m^{\bullet+}$ (n, m = even number). The results show that usually the cations $C_nH_{m+1}^+$ are more reactive than the neighboring radical cations $C_nH_m^{\bullet+}$ and $C_nH_{m+2}^{\bullet+}$ (see Table 1), if the general increase of reactivity with decreasing number of hydrogen atoms is taken into account. Thus, the cluster ions of highest reactivity in the series of ions $C_{18}H_x^+$ are the ions $C_{18}H_5^+$, while for $C_{20}H_x^+$ both ions $C_{20}H_5^+$ and $C_{20}H_4^{\bullet+}$ exhibit 100% reaction efficiency. Essentially, the cations $C_nH_{m+1}^+$ are polycyclic analogues of the phenyl cation $C_6H_5^+$ which is known to be a strong electrophile owing to its empty σ-orbital providing the positive charge.[35] Similarly, the positive charge of all polycyclic cations $C_nH_{m+1}^+$ is very likely localized in the empty σ-orbital of one of the former C−H bonds. The additional radical electrons in ions of low hydrogen content resulting from the other C−H bond cleavages may be either located in separated σ-orbitals at the rim of the polycyclic ring, or may combine to give an aryne-π bond in the case of a pair of neighboring electrons. In the latter case the ions $C_nH_{m+1}^+$ are true analogues of the phenyl cation, while in the former case the ion corresponds to a distonic "multiradical" cation with an even number of single electrons at the rim of the aromatic nucleus (Scheme 3). Recently it has been shown[20b] that these "multiradical" cation species prefer a singlet ground state and exhibit a rather low reactivity with respect to the radical electrons. Anyway, for both electronic configurations of the cations $C_nH_{m+1}^+$ it is reasonable to assume a carbenium cation reactivity (termed "C$^+$reactivity" in the following) which is controlled by the positive charge in an empty σ-orbital in analogy to the phenyl cation. This would explain the increased reactivity toward the nucleophilic DMDS.

In contrast to the cations $C_nH_{m+1}^+$, the radical cations $C_nH_m^{\bullet+}$ must naturally exist in a doublet state. If the ions exhibit an aryne structure, the positive charge and the radical electron reside in a single occupied π-orbital. Such ions exhibit a reduced

TABLE 2: Product Ion Distribution at the End of the Reaction of Hydrogenated Carbon Cluster Ions $C_nH_x^+$ with DMDS

Ion	n.r. (%)	CE (%)	$+CH_3S$ (%)	$+CH_3SH$ (%)	$+SSCH_3$ (%)	$+(CH_3S)_2$ (%)
$C_{18}H_9$(**1**)	7	39	47	3%	<1	<1
$C_{18}H_9$ (**2**)	19	27	40	6	3	6
$C_{18}H_9$ (**3**)	8	47	37	4	1	3
$C_{18}H_9$ (**4**)	12	14	62	5	3	4
$C_{20}H_9$ (**5**)	13	0	68	9	3	7

Ion	n.r. (%)	CE (%)	$+CH_3S$ (%)	$+CH_3SH$ (%)	$+SSCH_3$ (%)	$+(CH_3S)_2$ (%)
$C_{18}H_8$ (**1**)	43	14	2	15	9	12
$C_{18}H_8$ (**2**)	39	14	3	15	13	15
$C_{18}H_8$ (**3**)	30	29	3	18	7	14
$C_{18}H_8$ (**4**)	37	4	2	21	17	16
$C_{20}H_8$(**5**)	30	0	5	33	16	16

Ion	n.r. (%)	CE (%)	$+CH_3S^a$ (%)	$+CH_3SH$ (%)	$+SSCH_3$ (%)	$+(CH_3S)_2$ (%)	$+CH_2S$ (%)
$C_{18}H_7$ (**1**)	0	7	55	6	4	6	9
$C_{18}H_7$ (**2**)	0	23	49	11	4	3	9
$C_{18}H_7$ (**3**)	0	57	31	8	3	3	
$C_{18}H_7$ (**4**)	0	19	57	5	4	5	9
$C_{20}H_7$ (**5**)	0	20	59	5	5	5	3

Ion	n.r. (%)	CE (%)	$+CH_3S^b$ (%)	$+CH_3SH^c$ (%)	$+SSCH_3^d$ (%)	$+(CH_3S)_2$ (%)
$C_{18}H_6$ (**2**)	0	20	10	49	13	7
$C_{18}H_6$ (**1**)	0	7	17	53	15	6
$C_{18}H_6$ (**3**)	0	24	9	35	10	4
$C_{18}H_6$ (**4**)	4	16	12	45	16	6
$C_{18}H_6$ (**5**)	5	6	11	45	18	4

Ion	n.r. (%)	CE (%)	$+CH_3S^b$ (%)	$+CH_3SH^c$ (%)	$+SSCH_3^d$ (%)	$+(CH_3S)_2$ (%)
$C_{18}H_5$ (**1**)	0	24	35	10	11	16
$C_{18}H_5$ (**2**)	0	37	43	7	8	13
$C_{18}H_5$ (**3**)	0	23	47	6	13	8
$C_{18}H_5$ (**4**)	0	34	35	6	10	13
$C_{20}H_5$ (**5**)	0	45	26	11	17	6

Ion	n.r. (%)	CE (%)	$+CH_3S^e$ (%)	$+CH_3SH^e$ (%)	$+SSCH_3^e$ (%)	$+(CH_3S)_2$ (%)
$C_{18}H_4$ (**1**)	0%	32%	10%	38%	12%	<1%
$C_{18}H_4$ (**2**)	0%	20%	8%	60%	13%	<1%
$C_{18}H_4$ (**3**)	0%	24%	7%	55%	12%	<1%
$C_{18}H_4$ (**4**)	0%	26%	19%	43%	12%	<1%
$C_{20}H_4$ (**5**)	7%	42%	5%	30%	14%	<1%

[a] Secondary product ions ($+CH_3S+CH_3SH$) and ($+CH_3S+CH_3S_2$) included. [b] Secondary product ions ($+CH_3S+CH_3SH$) included. [c] Secondary product ions ($+2CH_3SH$), ($+CH_3SH+CH_3S$), and ($+CH_3SH+$DMDS) included. [d] Secondary product ion ($+CH_3S_2+CH_3S$). [e] Secondary product ions included, see Scheme 4.

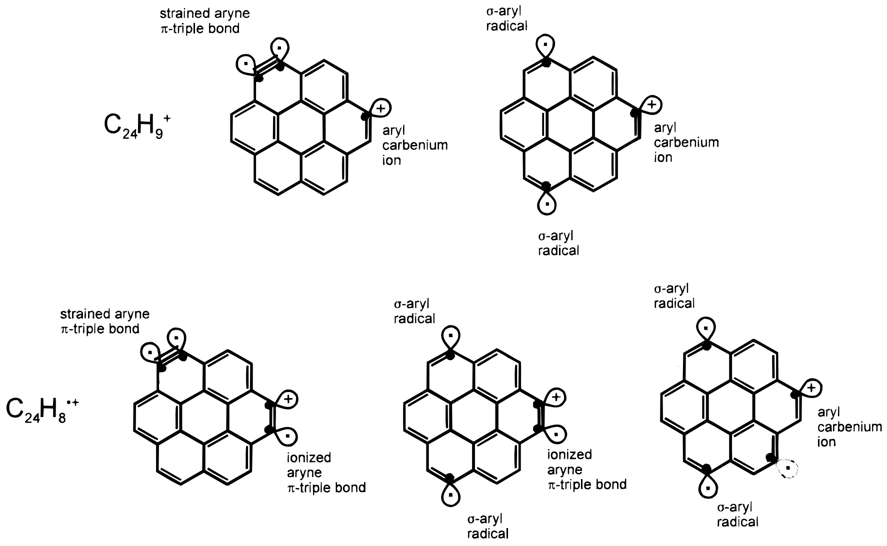
electrophilic character responsible for a reduced reactivity (termed "aryne reactivity" in the following) toward the nucleophilic DMDS. This reduced reactivity of radical cations is predicted by the configuration mixing model of Shaik et al.[36] and has been experimentally observed for the reaction of the radical cations of halogenated benzene with nucleophiles.[37] In the case of DMDS as reactant, the aryne radical cations may undergo charge exchange and addition to the reactive triple bond as possible reactions. If the positive charge and the radical electron are localized in separate σ orbitals, the ions $C_nH_m^{\bullet+}$ are distonic ions which are expected to show a separate reactivity toward DMDS.[20] This explanation attributes the dependence of the reactivity of the cluster ions $C_nH_x^+$ on the odd/even number x of H atoms to different electronic configurations of the ions, while the general increase of the reactivity with a decreasing number x of H atoms in the ions reflects obviously the increased exothermicity of the ion/molecule reaction due to the increasingly less stable cluster ions of low hydrogen content.

The different electronic properties of the cluster cations $C_nH_{m+1}^+$ and the cluster radical cations $C_nH_m^{\bullet+}$ are clearly reflected by different main product ions of the reaction with DMDS. Thus, the very rich chemistry shown by reactions of the ions $C_nH_x^+$, $n = 18, 20, 24$, with DMDS provides some information about the structures of these hydrogenated carbon cluster ions. It has to be remembered, however, that the almost equal chance to remove any of the H atoms during a single step of SORI−CID leads to the formation of isomers for each formula $C_nH_x^+$, especially in the case of ions which arise by loss of about half of the number of H atoms present in the parent PAH. The various electronic structural constituents of the cluster ions (an aryl carbenium ion, an aryl radical, and a strained triple aryne bond), which may be present, result in parallel reactions of different mechanisms. Besides charge exchange, either $CH_3S^\bullet$ abstraction from DMDS to form adduct ions $[C_nH_x(CH_3S)]^{\bullet+}$ or addition of CH_3SH to give products $[M+CH_3SH]^{\bullet+}$ is observed for all cluster ions as the main primary reaction. Further, secondary reactions with DMDS are observed, in particular, for cluster ions of low hydrogen content. These secondary reactions consist of either addition of $CH_3S^\bullet$ or CH_3SH to the primary product ions. Minor reactions are the addition of a complete molecule DMDS (or of two CH_3S groups) and of the fragment $CH_3SS^\bullet$. Of the primary reactions, the $CH_3S^\bullet$ abstraction is strongly preferred by the cations $C_nH_{m+1}^+$, while the radical cations $C_nH_m^{\bullet+}$ react mostly by primary addition of CH_3SH. It is of interest to note that in both cases the product ion $[M+CH_3S\bullet]^+$ and $[M+CH_3SH]^{\bullet+}$ corresponds to a radical cation.

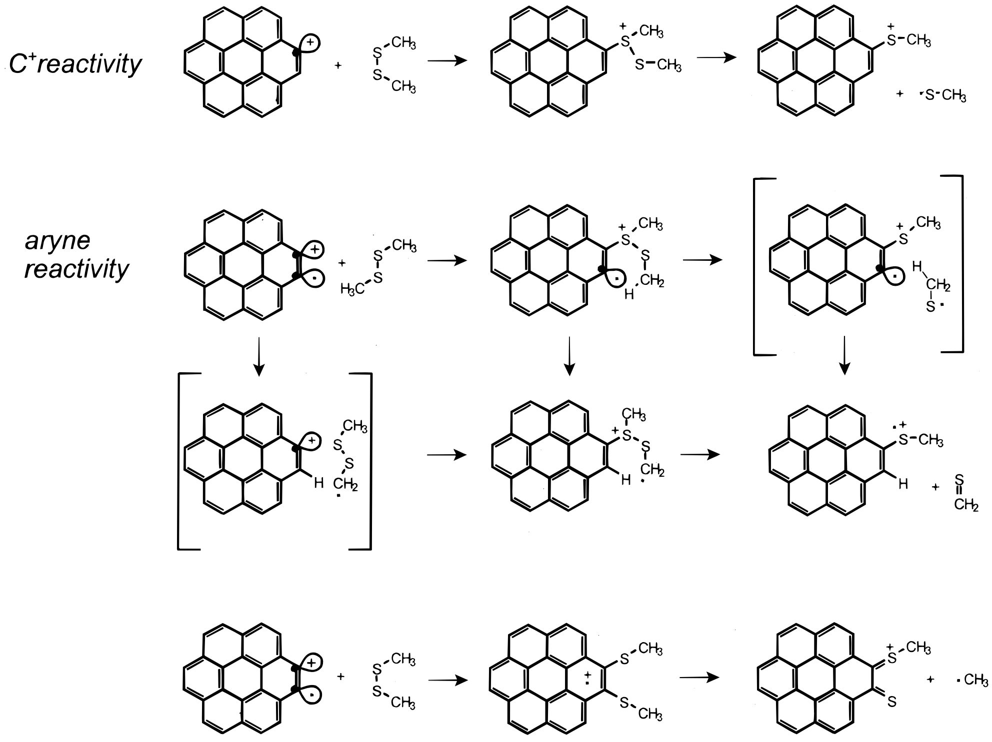
This different reactivity pattern (C^+ reactivity versus aryne reactivty) is most clearly observed for the reactions of cluster ions $C_{24}H_{11}^+$ and $C_{24}H_{10}^{\bullet+}$ from coronene **6**. As mentioned before, the "cluster ions" $C_{18}H_{11}^+$, $C_{18}H_{10}^{\bullet+}$, $C_{20}H_{11}^+$, and $C_{20}H_{10}^{\bullet+}$ generated by loss of H and 2 H, respectively, from the molecular ion of **1**−**5** do not react with DMDS, very likely because only endothermic reactions are possible. In contrast, the ions generated from **6** by loss of one and two H atoms do react quite effectively with DMDS (see Table 2). $C_{24}H_{11}^+$ is a "simple" aryl cation exhibiting only one reaction center, and $C_{24}H_{10}^+$ can be either a monoaryne radical cation or in ionized arylene diradical. Accordingly, both cluster ions should show only the prototypical C^+ reactivity of a carbenium cation or the prototypical aryne reactivity of a radical cation. This is indeed observed: $C_{24}H_{11}^+$ reacts completely by forming only the product ion $[M+CH_3S^\bullet]^+$, with little charge exchange (IE (coronene **6**) = 7.29 eV[33]), while $C_{24}H_{10}^{\bullet+}$ yields only $[M+CH_3SH]^{\bullet+}$, with some charge exchange and a fraction of unreactive ions $C_{24}H_{10}^{\bullet+}$. The suggested mechanisms of these reactions are depicted in Scheme 4.

The main reaction mechanism of the C^+ reactivity corresponds to nucleophilic addition of the aryl cation $C_{24}H_{11}^+$ to the lone pair at one of the S atoms of DMDS. This is certainly an exothermic reaction, occurring without a notable activation barrier, and hence gives rise to an energetically excited sulfonium ion. In FT-ICR, energetically excited product ions cannot escape dissociation because of the lack of an efficient stabilization process in the diluted gas phase. Consequently, dissociation of the addition product occurs either by retrogression into the reactants or by breaking the weak S−S bond of the adduct and eliminating a radical $CH_3S^\bullet$, resulting in the

SCHEME 3 . Possible Structures of Cations $C_{24}H_9^+$ and Radical Cations $C_{24}H_8^{\bullet+}$.



SCHEME 4 Proposed Reaction Mechanisms for C^+ Reactivity and Aryne Reactivity of the Cluster Ions $C_{24}H_{11}^+$ and $C_{24}H_{10}^+$, Respectively.



product ion $[C_nH_x^\bullet\ CH_3S]^{\bullet+}$. Since the structure of the ion $C_{24}H_{11}^+$ does not depend on the position of the H atom cleaved, no isomers and especially no unreactive component are observed. The reaction mechanisms of the aryne reactivity of the radical cation $C_{24}H_{10}^{\bullet+}$ with DMDS are obviously more complex. It has to be expected that the ions $C_{24}H_{10}^{\bullet+}$ are already a mixture of isomers, since the individual structure of the ions depends on the origin of the second H atom lost. This is most clearly substantiated by the observation of a fraction of ions unreactive toward DMDS. The *ortho*-didehydrocoronene radical cation is expected to be the most stable isomer of $C_{24}H_{10}^{\bullet+}$ because of stabilization by an (ionized) aryne triple bond, while the other isomers correspond to distonic radical cations of reduced stability. There are several mechanisms possible for the formation of the $[C_nH_x^\bullet CH_3SH]^{\bullet+}$ by reaction of the cluster ions with DMDS. The first one is a concerted abstraction of a CH_3S group and an H atom from DMDS by the radical cation $C_{24}H_{10}^{\bullet+}$. This mechanism is rather questionable on entropic reasons and appears feasible only for ions containing an ionized aryne bond. A stepwise addition of the CH_3S group and the H atoms is more likely, starting either by abstraction of the H atom from a methyl group of DMDS by the radical site of the ion $C_{24}H_{10}^{\bullet+}$ or, more plausibly, by addition of the carbenium center of the radical cation (the "electron hole" of the positive charge) to the lone pair at one of the S atoms of DMDS. In the first case, the H abstraction converts $C_{24}H_{10}^{\bullet+}$ into the aryl cation $C_{24}H_{11}^+$, and if the neutral product $^\bullet CH_2{-}S{-}S{-}CH_3$ still stays around in an electrostatically bound ion/neutral complex, the reaction can proceed to completion by electrophilic attack of the aryl cation on the S atom and elimination of thioformalde-

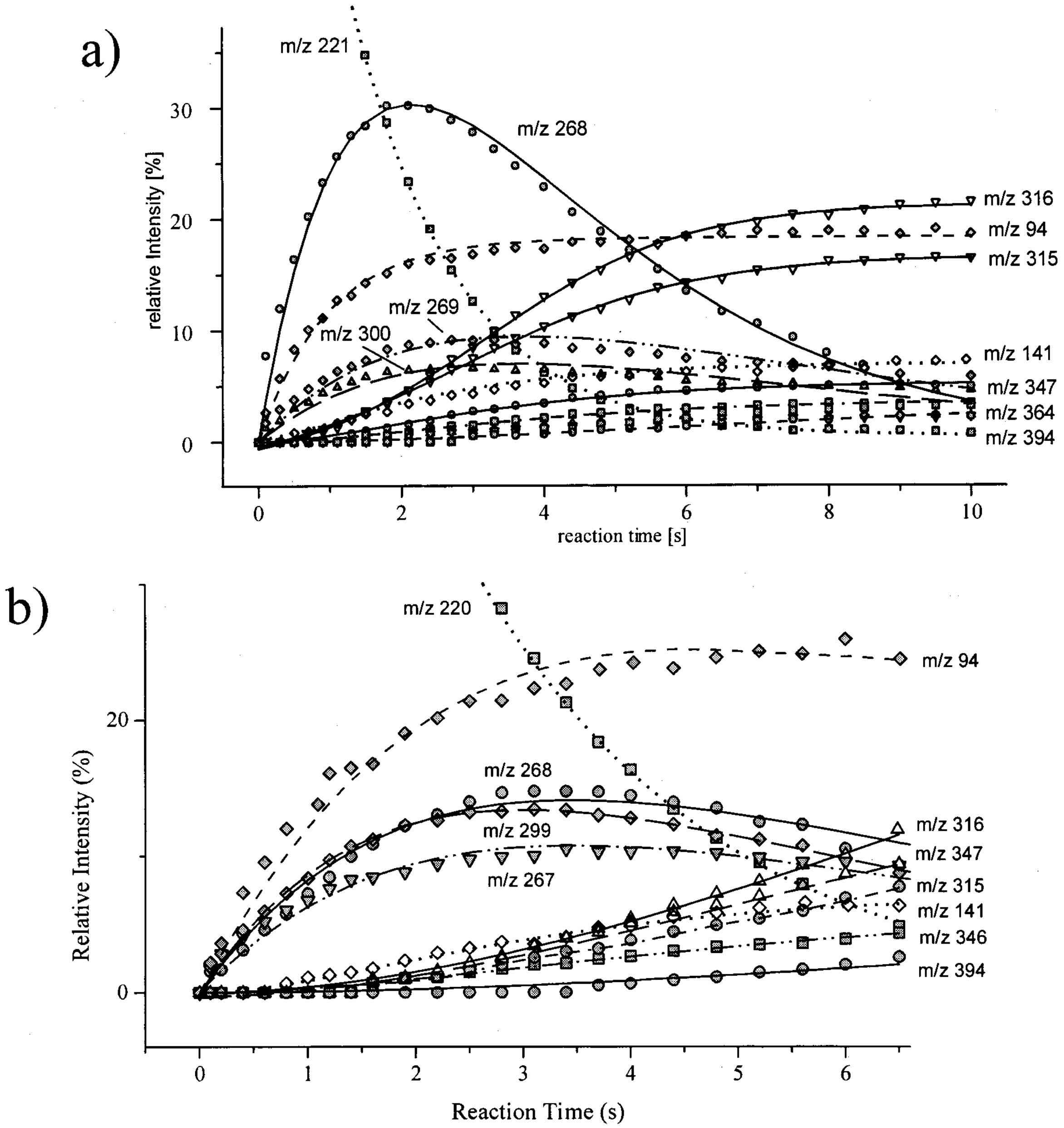
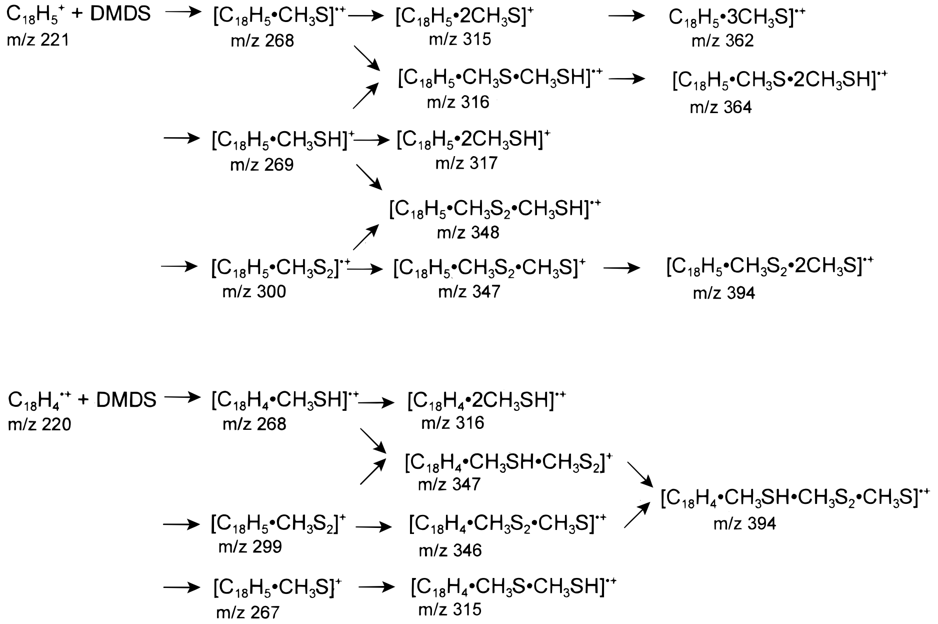


Figure 3. Kinetic plots for the reaction of cluster ions (a) $C_{18}H_5^+$, *m/z* 221, (b) $C_{18}H_4^{\bullet+}$, *m/z* 220, derived from **1**, with DMDS.

hyde $CH_2{=}S$. In the second case of an initial electrophilic addition of the carbenium center of $C_{24}H_{10}^{\bullet+}$, a distonic intermediate is generated consisting of a stable sulfonium group and a radical site corresponding to an aryl radical. Then, intramolecular H abstraction by this radical from a CH_3 group of the original DMDS moiety followed by elimination of $CH_2{=}S$ terminates the reaction.

A stepwise addition of CH_3SH is possible for all isomers of $C_{24}H_{10}^{\bullet+}$ if an intermediate ion/neutral complex allows the second step. This is particularly true for the mechanism involving initial H abstraction, while the initial electrophilic addition provides a distonic sulfonium ion as a covalently bonded intermediate, in which intramolecular H transfer can occur to a nearby radical site without requiring an intermediate ion/neutral complex. It is tempting to assume that this is the main mechanism, and that the fraction of unreactive ions observed for $C_{24}H_{10}^{\bullet+}$ (and the other cluster ions formed by elimination of only a few H atoms, see Table 2) corresponds to distonic isomers in which the positive charge and the radical site are at such a large distance that intramolecular H transfer in the last reaction step is not possible. However, as mentioned above, it is also possible that the unreactive ion $C_{24}H_{10}^{\bullet+}$ represents in fact the most stable isomer, *ortho*-didehydrocoronene radical ion, which can experience only endothermic reactions with DMDS. In this connection it may be of significance that the other two primary reaction products, formal addition of DMDS (or of two CH_3S moieties) and of a CH_3S_2 moiety, are not observed for ions $C_{24}H_{10}^{\bullet+}$. These product ions are usually also typical of the aryne reactivity, as can be seen from Table 2 by comparing the reaction products of ions $C_nH_9^+$ and $C_nH_8^{\bullet+}$, $n = 18, 20$. This addition of DMDS can be envisaged by a mechanism, shown also in Scheme 4, that is related to the mechanisms of addition of CH_3SH. The initial step is again the addition of the electrophilic carbenium center to a S atom, but in the second step the complete dissociating CH_3S radical is captured by the radical site of the radical ion $C_nH_m^{\bullet+}$. Because no neutral fragment is eliminated to carry off the excess energy of the exothermic process, the adduct ion $[C_nH_m(CH_3S)_2]^{\bullet+}$ is energetically excited and can fragment by elimination of a CH_3 radical from one of the SCH_3 groups,

SCHEME 5 Reaction Sequences of Cations $C_{18}H_5^+$ and Radical Cations $C_{18}H_4^{\bullet+}$ with DMDS.



producing the product ion $[C_nH_m(CH_3S_2)]^{\bullet+}$. The loss of methyl is a well-known fragmentation in the mass spectra of dimethyl ethers of dihydroxybenzenes and their thio analogues if the ether or thioether substituents are in an ortho or para position, which allows a resonance stabilization of the fragment ion. Thus is likely that the product ions $[C_nH_m(CH_3S)_2]^{\bullet+}$ and $[C_nH_m(CH_2S_2)]^+$ arise predominantly from those isomers of the cluster ions $C_nH_x^+$, which contain an aryne triple bond and give rise to ortho-substituted ions $[C_nH_m(CH_3S)_2]^{\bullet+}$. As mentioned earlier, reactions of this isomer of the ions $C_{24}H_{10}^{\bullet+}$ from **6** are presumably endothermic, so that no (formal) addition of DMDS and CH_3S_2 is observed in this case.

In principle, the different product patterns of C^+ reactivity and aryne reactivity are also observed for all of the other cluster ions $C_nH_x^+$, resulting in an increased intensity of product ions $[C_nH_{m+1}(CH_3S)]^{\bullet+}$ for cations and $[C_nH_m(CH_3S)_2]^{\bullet+}$ for radical cations (Table 2). However, with the decreasing number of H atoms in the cluster ions, the number of possible reaction centers (radical sites, strained aryne bonds) in the ions increases. As a consequence, secondary reactions of the primary product ions $[C_nH_{m+1}(CH_3S)]^{\bullet+}$ and $[C_nH_m(CH_3S)_2]^{\bullet+}$ become more and more important. For example, while the ion $[C_nH_9(CH_3S)]^{\bullet+}$ is still the only abundant reaction product of cluster ions $C_nH_9^+$, $n = 18, 20$, which arise after loss of 3 H atoms from the parent PAH, the product ion $[C_nH_7(CH_3S)]^{\bullet+}$ of the cluster ions $C_nH_7^+$, which arises by loss of 5 H atoms, undergoes already secondary reactions, mainly by addition of CH_3SH to generate the ion $[[C_nH_7(C_2H_7S_2)]^{\bullet+}$. In the case of lower hydrogenated cluster ions C_nH_x+, $x \leq 6$, the number of possible secondary and tertiary reactions by further addition of CH_3SH, $(2CH_3S)$, and CH_3S_2 increases, as shown in Figure 3 by the kinetic plots of the reactions of ions $C_{18}H_5^+$ and $C_{18}H_4^{\bullet+}$ derived from **1** and by the reaction sequences presented in Scheme 5. Since both primary product ions $[C_nH_{m+1}CH_3S)]^{\bullet+}$ and $[C_nH_mCH_3SH)]^{\bullet+}$ are radical cations, their further reactions with DMDS may proceed by mechanisms similar to those depicted in Scheme 3.

The typical product ions of the primary reactions of the cluster ions $C_nH_x^+$ derived by a stepwise loss of the H atoms from the molecular ions of polycyclic PAH with DMDS as well as the products of secondary reactions can be most conveniently explained by the presence of various reactive centers in the ions corresponding to the carbenium center of an aryl cation, of the strained C−C triple bond of an aryne, and of σ-type aryl radicals. This agrees with a conservation of the polycyclic carbon skeleton of the parent PAH in these cluster ions, as previously suggested from the results of a reaction of these hydrogenated carbon cluster ions with benzene.[19]

Conclusion

The results of this study of the ion/molecule reactions of the hydrogenated carbon cluster ions $C_nH_x^+$, with DMDS demonstrate some interesting points of the gas-phase ion chemistry of such cluster ions.

(1) The different bimolecular rate constants and intensity distribution of product ions of the reactions of the four series of ions $C_{18}H_x^+$, which were generated from isomeric PAH **1**−**4**, with DMDS confirm the earlier observation from their reaction with benzene[19] that these cluster ions retain different structures, even in the case of ions of a low hydrogen content which have suffered collisional activation for several times to eliminate up to eight hydrogen atoms.

(2) Generally, the bimolecular rate constant of the reaction with DMDS increases in each series with decreasing number of hydrogen atoms of the ion. This is again parallel to the reaction with benzene.[19] The most apparent explanation for this effect is a decreasing stability of the ions with decreasing number of hydrogen atoms. This makes all of the reactions of ions with low hydrogen content more exothermic.

(3) Besides increasing with decreasing hydrogen content, the bimolecular rate constants of the reactions with DMDS oscillate between ions $C_nH_x^+$ with even and odd number of hydrogen atoms. Ions containing an odd number of hydrogen atoms correspond to even electron carbenium ions analogous to the phenyl cation and related aryl cations, while ions with an even number of hydrogen atoms correspond to arene and dehydroarene radical cations with an odd number of electrons. This different electronic configuration is reflected in a different reactivity, and, in the case of DMDS as reactant, the even electron aryl cations are more reactive than the neighboring radical cations of the series.

(4) The different reactivity of even and odd electron cluster ions $C_nH_x^+$ is more obvious in the reaction with DMDS than in

the reaction with benzene[19] because of the rich chemistry of the system $C_nH_x^+$/DMDS. Odd and even electron ions result in different main products of the reaction with DMDS, i.e., addition of a $CH_3S^\bullet$ radical by aryl cations and addition of CH_3SH by dehydroarene radical cations. Although these reaction products differ from those commonly observed in the reactions of organic radical cations and distonic ions with DMDS, these and other product ions of the systems $C_nH_x^+$/DMDS can be linked without much effort to reactive centers within the ions which are expected to be formed if the cluster ions $C_nH_x^+$ retain the carbon skeleton of the parent PAH while losing hydrogen atoms from the rim of the aromatic nucleus.

Accordingly, the present results corroborate the assumption that cluster ions $C_nH_x^+$ and probably also "pure" carbon cluster ions $C_n^{\bullet+}$ containing between 18 and 24 carbon atoms do exist as graphitic structures and can be prepared by suitable methods from PAH and their derivatives. This does not mean that the graphitic cluster ions represent the most stable structure of carbon cluster ions of this size. Rather it has to be assumed that large activation barriers separate the graphitic carbon cluster ions from their likely more stable isomers of monocyclic structure. Hence, if the cluster ions are prepared by a "soft" technique the graphitic structures of the precursors are preserved, while preparation using a "hard" technique such as laser evaporations induces isomerization into more stable structures.

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(30) For simplicity, k_{bi} corresponds in the case of the hydrogen-rich species $C_nH_x^+$, ($x = 9, 8$) to some mean value calculated by using a pseudo-first-order fit to the data of the kinetic plot. Further, the "end of reaction" refers here to the disappearance of the initial reactive ions $C_nH_x^+$ by primary reaction with DMDS. Secondary reactions may still continue.

(31) It has been suggested by a referee that the observation of a fraction of reactive and (almost) unreactive ions $C_nH_x^+$, ($n = 18, 20$; $x = 9, 8$) is not due to ions of different structures but due to the presence of excited ions which have survived collisional cooling with argon prior to reaction with DMDS. Ions $C_nH_x^+$ of sufficient internal energy may undergo endothermic ion/molecule reactions with DMDS in competition with deactivation by unreactive collisions with DMDS, and after deactivation the ions $C_nH_x^+$ do not exhibit any reaction with DMDS. In fact, some "hot ions" may be present (see discussion of charge exchange), but deactivation by collision with DMDS is obviously quite effective and does not extend over a period of 4−6 s, as seen for the reactions of $C_nH_x^+$, ($x = 9, 8$). Further, it is difficult to understand why long-lived excited ions should be only formed in the case of $x = 9, 8$, while for ions $C_nH_x^+$, ($x \leq 7$) the kinetic plots do not exhibit any deviation from pseudo-first-order kinetics. Since the rate constant of an ion/molecule reaction depends on the amount of internal energy of the ion, slow deactivation in competition with reaction with DMDS should induce such deviations.

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