Ion/Molecule Reactions of Carbon Cluster Ions and Acrylonitrile

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Abstract: Ion/molecule reactions of carbon cluster ions ($C_n^{\bullet+}$, $n = 10–18$ and 20) in the gas phase with acrylonitrile (ACN) as the neutral reagent were investigated by Fourier transform ion cyclotron resonance spectrometry (FT-ICR). The carbon cluster ions studied were generated by electron impact ionization of perchlorinated polyaromatic compounds (PPA) and subsequent exhaustive chlorine elimination in the external ion source of the FT-ICR spectrometer. The precursor PPA were prepared by chlorination of the appropriate polyaromatic hydrocarbons using the BMC reagent. The only reaction observed for $C_n^{\bullet+}$ was the formation of adduct ions stabilized by radiative association (for $n = 10–18$ and 20) with the exception of $C_{16}^{\bullet+}$ which stabilized the adduct ion by loss of a neutral C_3. The rate constants for the reaction of $C_n^{\bullet+}$ with ACN vary from $k_{bi} = <10^{-13}$ cm^3 molecule^{-1} s^{-1} ($C_{18}^{\bullet+}$, $C_{20}^{\bullet+}$) to $k_{bi} = 7.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} ($C_{13}^{\bullet+}$) and are distinctly larger than with HCN and C_2H_4 studied before. $C_{13}^{\bullet+}$ and $C_{17}^{\bullet+}$ exhibit extraordinary reactivity with ACN. For structural information about the product ions $C_{n+3}H_3N^{\bullet+}$ formed from $C_n^{\bullet+}$ and ACN, collision induced dissociation (CID) spectra were obtained by collision of the accelerated product ions of the ion/molecule reactions with argon gas in the FT-ICR cell for two product ions of sufficient large abundances. In addition, the deprotonation of $C_{n+3}H_3N^+$ ($n = 10, 13$) product ions by a series of reference bases was studied resulting in a proton affinity of c. 822 and 815 kJ/mol for the conjugate bases $C_{13}H_2N$ and $C_{16}H_2N$, respectively.

Introduction

Carbon cluster ions $C_n^{\bullet+}$ have been investigated extensively during the last years[1] because of their probably important role in astrochemistry[2] and combustion processes.[3] There are several sources and experimental techniques, which have been used to create and study carbon cluster ions.[4] The technique most often used is the laser evaporation of graphite, allowing to generate neutral clusters and cluster ions varying in size from a small number of C atoms to clusters containing hundreds of C atoms. Under special conditions even macroscopic quantities of C_{60} are generated by the laser evaporation technique.[4b] Carbon cluster ions are also prepared by electron impact induced dissociation from suitable precursors.[5] In earlier studies using this technique, the size of the carbon cluster ions produced was limited to about $n = 6$, but recently it was shown that also larger carbon cluster ions may be generated by electron impact induced fragmentation of appropriate perchlorinated organic compounds.[6] Perchlori-

nated polycyclic aromatic compounds (PPA) proved to be particularly suitable to prepare gaseous carbon cluster ions. The PPA are synthesized conveniently from the corresponding polyaromatic hydrocarbon by chlorination using the so called "BMC reagent"[7] and by photochlorination. Thus, carbon cluster ions $C_n^{\bullet+}$ with $n = 10–20$ or even larger are accessible.

There are several interesting aspects of generation of carbon cluster ions by electron impact induced fragmentations of organic molecules. Firstly, it appears feasible to produce by this method cluster ions with an even as well as an odd number of C atoms, some of which are formed only in low abundances by laser evaporation. Secondly, this method is adapted easily to conventional mass spectrometric equipment. Finally, carbon prefers covalent bonding, and this leads to specific structures of carbon clusters and their molecular ions. The most fascinating consequence of this preference for covalent bonding is the spherical structure of the fullerenes made from six- and five-membered rings.[8] In the case of smaller neutral and ionized carbon clusters, there is theoretical and experimental evidence for linear, cyclic, and polycyclic structures and for cluster isomers.[8,9,11] Therefore, it is of interest to generate carbon cluster ions by different techniques to test the possible formation of isomers. In this regard formation of carbon cluster ions by electron impact induced

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Chart I
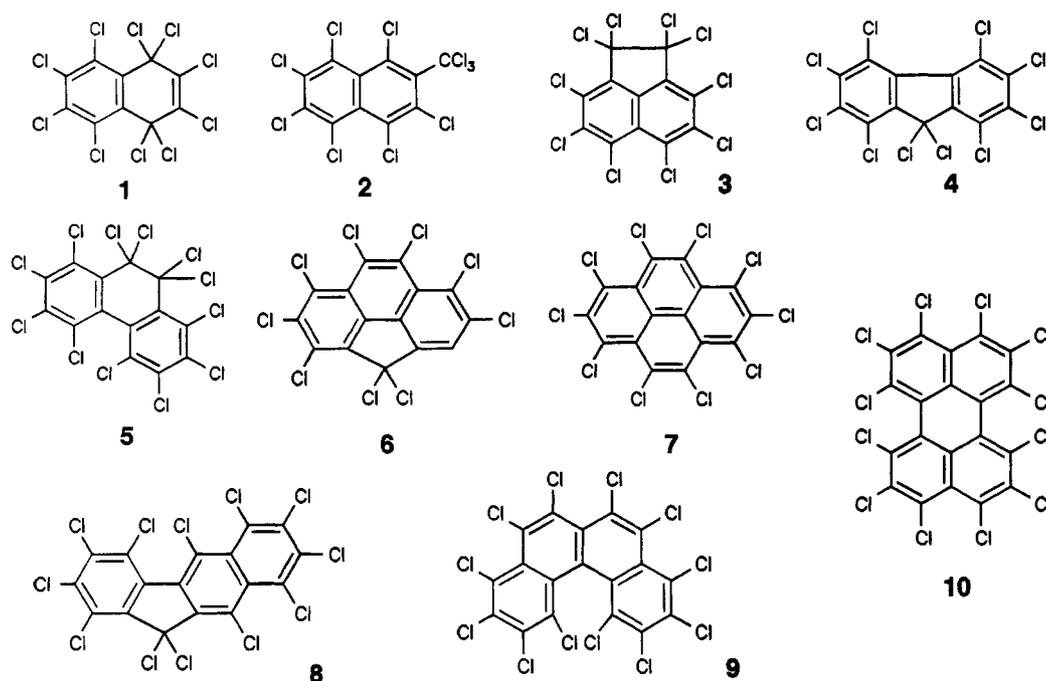
fragmentation of a precursor with a definite structure is of special interest because part or all of the initial carbon backbone of the precursor may survive the ionization and fragmentation processes leading to a "memory effect" of the resulting carbon cluster ions. Thus, this method may contribute to a better understanding of the structures of small carbon clusters.

A study of ion/molecule reactions of carbon cluster ions is especially informative about the structures and the structure/reactivity relationship of these covalent clusters.[10] Fourier transform ion cyclotron resonance spectrometry (FT-ICR)[11-13] and selected ion flow tube (SIFT) techniques[2] have been used successfully to study reactions of carbon cluster ions in the gas phase. FT-ICR[14] is not only well suited for measurements at high mass ranges and by high resolution but is also suitable for the study of slow ion/molecule reactions owing to the long residence time of the ions possible in the ICR cell. In addition and because of the low operating pressure necessary to achieve optimal performance, the conditions of ion/molecule reactions in the ICR cell are similar to the interstellar environment where stabilization of an ion/neutral encounter complex by third body collisions is negligible. Hence, the FT-ICR technique is the method of choice to study the formation of organic species in interstellar clouds.

Studies of ion/molecule reactions of carbon cluster ions $C_n^{\bullet+}$ have provided evidence that $C_n^{\bullet+}$ with $n < 10$ have a linear structure and are more reactive than cyclic $C_n^{\bullet+}$ with $n > 9$.[11b] Interestingly, alternating reactivities of carbon cluster ions $C_n^{\bullet+}$ with n even or odd were observed with some organic substrates.[11] This is a clear indication that carbon cluster ions exhibit the strong dependence of reactivity on structure typical for organic chemistry. To extend these studies by using a different technique for the preparation of the carbon cluster ions and using new reactants we have started a study of the ion/molecule reactions of $C_n^{\bullet+}$ with n in the range between 10 and 36 by FT-ICR. In

this paper we report results for the reaction of cluster ions $C_n^{\bullet+}$ ($n = 10$–18 and 20) with acrylonitrile $CH_2=CHCN$ (ACN).

Experimental Section

Compounds. Perchlorinated, 1,4-dihydronaphthalene 1, 2-methylnaphthalene 2, acenaphthene 3, fluorene 4, 9,10-dihydrophenanthrene 5, 4,5-methanophenanthrene 6, pyrene 7, 2,3-benzofluorene 8, 3,4-benzophenanthrene 9, and perylene 10 were prepared by chlorination of the corresponding polyaromatic hydrocarbon using the following conditions.

Perchlorinated compounds 3 and 5–10 were obtained by dissolving the aromatic hydrocarbon in the BMC reagent consisting of a mixture of S_2Cl_2 and $AlCl_3$ in a Cl equivalent ratio of 1:0.5 in 150 mL of SO_2Cl_2 and heating to 64 °C for 4 h. At the end of the reaction, the mixture was treated with icy water. After neutralization with $NaHCO_3$ the product was filtered or extracted with $CHCl_3$. Compounds 1 and 2 were obtained by chlorination of naphthalene and 2-methylnaphthalene, respectively, with Cl_2 and Fe powder in SO_2Cl_2 solution at 64 °C. The reaction mixture was hydrolyzed with cold water and extracted with dichloromethane. The extract was dried with $MgSO_4$, the solvent was removed by evaporation, and the residue was recrystallized from dichloromethane. The same procedure using fluorene resulted in a mixture of $C_{13}HCl_9$ and $C_{13}Cl_{10}$, which was transformed into compound 4 by photochlorination with Cl_2 in tetrachloromethane and recrystallized from dichloromethane. All products were purified by recrystallization or column chromatography on silica gel. The identification of all compounds was performed by 70-eV electron impact mass spectra and ^{13}C NMR spectra.

Decachloro-1,4-dihydronaphthalene (1) from 5.0 g (39 mmol) of naphthalene: yield 12.5 g (26.3 mmol, 67.5%), colorless crystals, mp 195 °C dec; MS (70 eV) m/z (%) = 470 (4.4%) $[M^{\bullet+}]$, 472 (10.0%), 474 (13.6%), 476 (8.4%), 478 (9.2%), 480 (3.1%); base peak m/z 404 $[(M - 2Cl^{\bullet+}]$; ^{13}C NMR (300 MHz, CDCl₃) $\delta = 138.9(q), 134.0(q), 132.4(q), 130.8(q), 79.5(q)$.

2-(Trichloromethyl)heptachloronaphthalene (2) from 5.0 g (35.2 mmol) of 2-methylnaphthalene: yield 1.0 g (2.1 mmol, 5.8%) after column chromatography (first fraction) on silica gel using *n*-pentane as eluent. The second fraction contained 1 (1.8 g), the other fractions the partially chlorinated fluorenes $C_{11}HCl_{11}$ (1.5 g, mp 208–210 °C) and $C_{11}H_2Cl_{10}$ (1.3 g; mp 180–182 °C. 2: Colorless crystals, mp 121–123 °C; MS (70 eV) m/z (%) = 482 (6.8%) $[M^{\bullet+}]$, 484 (22.0%), 486 (33.4%), 488 (24.1%), 490 (15.0%), 492 (6.0%); base peak m/z 451 $[(M - Cl)^+]$; ^{13}C NMR (300 MHz, CDCl₃) $\delta = 144.8(q), 139.0, 136.6(q), 134.0(q), 132.7(q), 130.6(q), 130.3(q), 125.5(q, 2 C atoms), 119.0(q), 81.5(q)$.

Decachloroacenaphthene (3) from 3.0 g (19.7 mmol) acenaphthylene: yield 0.9 g (1.8 mmol, 27%), pale yellow crystals, mp 252–253 °C; MS (70 eV) m/z (%) = 494 (4.5%) $[M^{\bullet+}]$, 496 (15.4%), 498 (23.0%), 500

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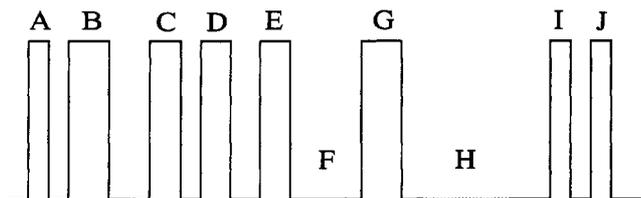
Figure 1. Pulse sequence used in FT-ICR: (A) quench pulse, (B) ionization, (C) swept frequency ejection, (D) single shots, (E) Ar pressure pulse, (F) thermalization delay, (G) single shots, (H) reaction delay, (I) excitation, and (J) detection.

(15.1%), 502 (8.1%), 504 (3.9%), 506 (1.7%); base peak m/z 463 [(M − Cl)$^+$]; ^{13}C NMR (300 MHz, CDCl$_3$) δ = 137.8(q) 134.3(q), 131.8(q), 131.1(q), 128.8(q), 123.9(q), 94.1(q).

Decachlorofluorene (4) from 1.00 g (6.0 mmol) of fluorene: yield 0.45 g (0.88 mmol, 35%), pale yellow crystals, mp 255–257 °C; MS (70 eV) m/z (%) = 506 (2.1%) [M$^{•+}$], 508 (5.4%), 510 (6.7%), 512 (9.6%), 514 (7.6%), 516 (3.7%), 518 (2.6%); base peak m/z 475 [(M − Cl)$^+$]; ^{13}C NMR (300 MHz, CDCl$_3$) δ = 142.0(q), 137.8(q), 136.3(q), 133.2-(q), 130.4(q), 127.3(q), 80.9(q).

Dodecachloro-9,10-dihydrophenanthrene (5) from 1.0 g (5.6 mmol) of phenanthrene: yield 1.8 g (3.0 mmol, 54%), colorless crystals, mp 295–300 °C dec; MS (70 eV) m/z (%) = 588 (14.0%) [M$^{•+}$], 590 (20.8%), 592 (49.3%), 594 (37.3%), 596 (27.4%), 598 (21.0%), 600 (6.1%); base peak m/z 557 [(M − Cl)$^+$].

Decachloro-4,5-methanophenanthrene (6) from 1.0 g (5.3 mmol) of 4,5-methanophenanthrene; yield 2.2 g (4.1 mmol, 76%), colorless crystals, mp c 305 °C dec; MS (70 ev) m/z (%) = 530 (2.5%) [M$^{•+}$], 532 (7.0%), 534 (10.3%), 536 (5.1%), 540 (2.0%); base peak 499 [(M − Cl)$^+$].

Decachloropyrene (7) from 1.0 g (5.0 mmol) of pyrene: yield 0.5 g (0.85 mmol, 17%), yellow crystals, mp 262–265 °C; MS (70 eV) m/z (%) = 542 (20.7%) [M$^{•+}$], 544 (62.3%), 546 (100%), 548 (84.0), 550 (48.1%), 552 (19.8%), 554 (6.6%), 556 (2.0%); ^{13}C NMR (300 MHz, CDCl$_3$) δ = 137.6 (q), 131.3 (q), 130.6 (q), 125.8 (q), 124.7 (q).

Dodecachloro-2,3-benzofluorene (8) from 0.5 g (2.3 mmol) 2.3-benzofluorene: yield 1.0 g (1.6 mmol, 69%), yellow crystals, mp c 300 °C dec; MS (70 ev) m/z (%) = 624 (1.8%) [M$^{•+}$], 626 (7.0%), 628 (11.5%), 630 (11.8%), 632 (9.2%), 634 (4.8%); base peak 593 [(M − Cl)$^+$].

Dodecachloro-3,4-benzophenanthrene (9) from 2.2 g (9.6 mmol) of 3,4-benzophenanthrene: The reaction with the BMC reagent results in the dihydroderivative C$_{18}$H$_2$Cl$_{14}$ which was converted into 9 by heating. Yield 0.43 g (0.67 mmol, 6.5%), brown-yellow crystals, mp 240–243 °C; MS (70 ev) m/z (%) = 636 (15.8%) [M$^{•+}$], 638 (55.2%), 640 (93.8%), 642 (100%), 644 (77.9%), 646 (40.3%), 648 (15.9%), 650 (4.9%), 652 (1.6%), 654 (1.1%).

Dodecachloroperylene (10) from 1.0 g (4.0 mmol) of perylene: yield 1.9 g (2.9 mmol, 74%), yellow-orange crystals, mp > 360 °C; MS (70 ev) m/z (%) = 660 (10.1%) [M$^{•+}$], 662 (52.3%), 664 (92.8%), 666 (100%), 668 (72.0%), 668 (37.8%), 670 (14.6%), 672 (14.6%), 674 (4.5%), 676 (1.1%).

The ^{13}C NMR spectra of 5, 6, and 8–10 were not measured because these compounds are not enough soluble in CDCl$_3$ and other solvents suitable for NMR.

FT-ICR Spectrometry. The carbon cluster ions studied were generated by electron impact ionization of the respective PPA in the external ion source[15] of a Bruker CMS 47X FT-ICR spectrometer.[16] The 70-eV mass spectra of 1–10 exhibit a distinct peak at the m/z value of the corresponding ion C$_n^{•+}$. According to high mass resolution measurements this peak is at least predominantly due to the ions C$_n^{•+}$ (Table I), which arise from consecutive and exhaustive chlorine elimination from the PPA molecular ions. The details of the PPA mass spectrometry are discussed elsewhere.[17]

Following the electron impact induced ionization and fragmentation the ions were transferred into the FT-ICR cell, and the experiment was performed using the pulse sequence shown in Figure 1.

Following a quench pulse to remove all ions from the ICR cell, ions formed in the external ion source were transferred by a 3-kV accelerating/

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Table I. Electron Impact Induced Formation of Cluster Ions C$_n^{•+}$ from PPA 1–10

C$_n^{•+}$	m/z	rel int[a] (%)	interference	ratio[b]
C$_{10}^{•+}$	120	10.4	C$_4^{35}$Cl^{37}Cl$^{•+}$	4.8/100
C$_{11}^{•+}$	132	8.9	C$_5^{35}$Cl^{37}Cl$^{•+}$	15.1/100
C$_{12}^{•+}$	144	21.5	C$_{12}^{35}$Cl$_2^{37}$Cl$_2^{2+}$	48.8/100
C$_{13}^{•+}$	156	13.7	C$_7^{35}$Cl^{37}Cl$^{•+}$	16.8/100
C$_{14}^{•+}$	168	18.4	C$_8^{35}$Cl^{37}Cl$^{•+}$	21.0/100
C$_{15}^{•+}$	180	11.2	C$_9^{35}$Cl^{37}Cl$^{•+}$	11.3/100
C$_{16}^{•+}$	192	15.7	C$_{10}^{35}$Cl^{37}Cl$^{•+}$	13.4/100
C$_{17}^{•+}$	204	8.6	C$_{16}^{35}$Cl$_3^{37}$Cl$_3^{2+}$	14.0/100
C$_{18}^{•+}$	216	13.1	C$_{18}^{35}$Cl$_3^{37}$Cl$_3^{2+}$	65.0/100
C$_{20}^{•+}$	240	7.8		

[a] Intensity relative to the base peak of the 70 eV mass spectrum. [b] Intensity of the interference ion relative to C$_n^{•+}$.

decelerating potential into the ICR cell. The ions were trapped by a trapping potential of approximately 1 V to minimize the kinetic energy of ions trapped. The carbon cluster ions to be studied were isolated by removing all other ions by broad band (BB or swept frequency) ejection and single radiofrequency (rf) pulses at selected frequencies (single shots, SS). This isolation of the ions C$_n^{•+}$ is difficult because of the interference ions at the same mass number (see Table I) and has to be performed with a "front-end" mass resolution of >4000. While this resolution is well within the high mass resolution capability of the FT-ICR instrument, an ejection at this small mass difference may lead to unintentional kinetic excitation of the isolated cluster ions. In order to minimize the off-resonance[18] cyclotron excitation of the ions isolated, the duration of the SS pulse was set to $1/(\nu_0 - \nu)$, where ν_0 is the frequency of the excitation field, which equals the ion cyclotron frequency of the neighboring ions to the ejected one, and ν corresponds to the ion cyclotron frequency of the ions selected. After isolation of the carbon cluster ions a pulsed valve was opened for 14 ms to allow a pressure pulse of Ar to enter the ICR cell for thermalizing the ions C$_n^{•+}$ for 1–3 s, during which the Ar pressure reached its maximum (ca. 10^{-5} mbar). This was followed by SS ejections to remove any reaction product ions (also from charge transfer) formed during this time. Then, a variable delay time was used to permit ion/molecule reactions to occur. Normally, the reaction period was varied from 1 s up to 60 s depending on reaction rate.

For each of the reaction times chosen, a broad band time domain signal containing of up to 100 experimental cycles was averaged, and this time domain data set was zero filled twice prior to performing Fourier transformation. Identical peak shapes were achieved after Fourier transformation by Gaussian multiplication of the time domain signal. This ensures proportionality of the peak height and peak area. Reaction constants were determined by observing the decrease of the reactant ion intensity relative to that of the total ions as a function of reaction time.

The ion/molecule reactions of the carbon cluster ions took place at a constant neutral reactant gas pressure of 1.4–14 × 10^{-8} mbar[19] and a temperature of 300 K. In Figure 2 the intensity/time curves obtained for the reactions of C$_{13}^{•+}$ and C$_{16}^{•+}$, respectively, with ACN are shown as typical examples. The pseudo-first-order reaction rate constant k_{exp} was extracted from the experimental intensity vs reaction time curve by fitting of a calculated curve. A good fit was always obtained without any indication of a bimodal reaction behavior. k_{exp} was converted to the bimolecular rate constant k_{bi} by accounting for the number density of the neutral reactant in the FT-ICR cell derived from the reactant gas pressure. The pressure reading of the ionization gauge close to the high vacuum pump for the FT-ICR cell was calibrated by rate measurements of the reactions CH$_4^{•+}$ + CH$_4$ → CH$_5^+$ + $^•$CH$_3$ (k = 1.5 × 10^{-9} cm^3 molecule^{-1} s^{-1} [20]) and NH$_3^{•+}$ + NH$_3$ → NH$_4^+$ + $^•$CH$_3$ (k = 2.2 × 10^{-9} cm^3 molecule^{-1} s^{-1} [21]). The sensitivity of the ionization gauge toward ACN (and other gases used) was determined by a standard method.[22] An error of 20% was estimated for k_{bi} and is mainly due to inexactness of the pressure measurements. The reaction efficiency (eff %) was obtained from the

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b
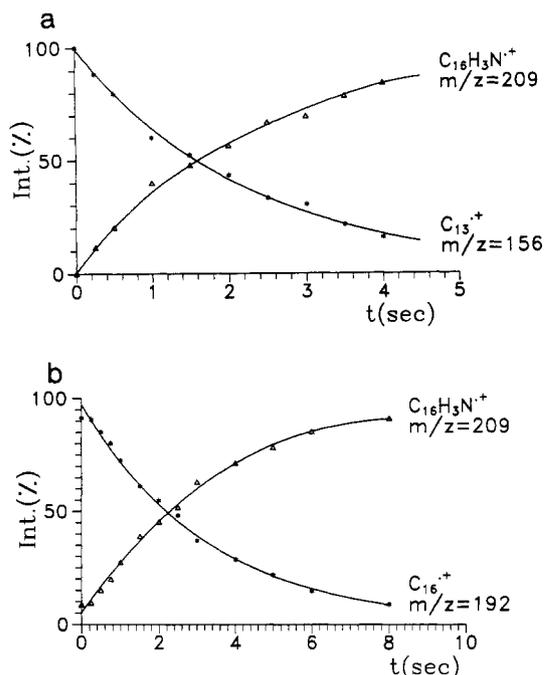
Figure 2. Rate curves for the reaction of carbon cluster ions $C_n^{\bullet+}$ with ACN: (a) $C_1^{\bullet+}$, $p_{ACN} = 3.7 \times 10^{-8}$ mbar and (b) $C_{16}^{\bullet+}$, $p_{ACN} = 1.3 \times 10^{-6}$ mbar.

ratio of the experimental k_{bi} to the theoretic rate constant k_c, which was evaluated according to the formula of Su and Chesnavich.[23]

To obtain structural information about the product ions of the reactions of $C_n^{\bullet+}$ with ACN, collision induced dissociation (CID)[24] of the product ions was achieved by accelerating the ions in argon gas. The following pulse sequence was executed in this case: (a) isolation and relaxation of carbon cluster ion $C_n^{\bullet+}$, (b) reactant gas pulse and ion/molecule reaction delay, (c) isolation of the target ion (product ion) for CID, (d) acceleration of the target ion, (e) argon pressure pulse and CID delay, and (f) excitation and detection.

The ions $C_n^{\bullet+}$ were reacted with ACN as described before, but the neutral ACN gas was introduced into the ICR cell by a pulsed valve for the ion/molecule reaction to occur. After a reaction delay and pumping away the ACN for 2–3 s, the target ions (product ions or parent $C_n^{\bullet+}$) were isolated by SS ejections of all other ions. This was followed by a short rf pulse (5–12 μs, $V_{p-p} = 126$ V) at the exact cyclotron frequency of the isolated target ion to increase its kinetic energy. Before collision with the pulsed Ar gas (maximal pressure 10^{-5} mbar), the product ions formed by charge-transfer reactions between the accelerated $C_n^{\bullet+}$ and any ACN still present in the FT-ICR cell were removed by the frequency sweep ejection technique. Then, dissociation of the parent ion occurred during the subsequent CID delay. In order to obtain abundant fragment ions, the kinetic energy of the accelerated ion was increased by altering the duration of the rf pulse while keeping its amplitude constant until at least half of the target ions had dissociated. The fragment ions and target ions were detected in the broad band mode.

Additional important information about the product ions of the reactions of $C_n^{\bullet+}$ with ACN was obtained by observing proton-transfer reactions to reference bases. These experiments were performed by modifying the CID pulse sequence as shown: (a) isolation and relaxation of carbon cluster ion $C_n^{\bullet+}$, (b) reactant gas pulse and ion/molecule reaction delay, (c) isolation of the product ion for deprotonation, (d) reference base pressure pulse and reaction delay, and (e) excitation and detection.

The acceleration of the product ions in step (d) was omitted, and argon gas in step (e) was replaced by the gaseous reference base. The deprotonation of the product ion from $C_n^{\bullet+}$ and ACN was followed for 3 s to distinguish between a fast exothermic proton transfer (reaction efficiency >50%) and a slow endothermic one (reaction efficiency <5%).

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Table II. Products and Rate Constants k_{bi} of the Reactions $C_n^{\bullet+}$ + CH$_2$=CHCN

educt ion	m/z	products	m/z	$k_{bi}10^{-12\ a}$	eff (%)
$C_{10}^{\bullet+}$	120	$C_{13}H_3N^{\bullet+}$	173	280	9.20
$C_{11}^{\bullet+}$	132	$C_{14}H^3N^{\bullet+}$	185	56	1.86
$C_{12}^{\bullet+}$	144	$C_{15}H_3N^{\bullet+}$	197	70	2.30
$C_{13}^{\bullet+}$	156	$C_{16}H_3N^{\bullet+}$	209	710	24.3
$C_{14}^{\bullet+}$	168	$C_{17}H_3N^{\bullet+}$	221	25	0.85
$C_{15}^{\bullet+}$	180	$C_{18}H_3N^{\bullet+}$	233	12^b	0.41
$C_{16}^{\bullet+}$	192	$C_{16}H_3N^{\bullet+}$ + C_3	209	9.3	0.32
$C_{17}^{\bullet+}$	204	$C_{20}H_3N^{\bullet+}$	257	200	7.0
$C_{18}^{\bullet+}$	216	$C_{21}H_3N^{\bullet+}$	269	<0.1	
$C_{20}^{\bullet+}$	240	$C_{23}H_3N^{\bullet+}$	293	<0.1	

[a] Cm^3 molecule^{-1} s^{-1}. [b] 56% of the ions $C_{15}^{\bullet+}$ are unreactive.

Results and Discussion

The carbon cluster ions studied are $C_{10}^{\bullet+}$ from perchloro-1,4-dihydronaphthalene **1**, $C_{11}^{\bullet+}$ from 1-(trichloromethyl)heptachloronaphthalene **2**, $C_{12}^{\bullet+}$ from perchloroacenaphthene **3**, $C_{13}^{\bullet+}$ from perchlorofluorene **4**, $C_{14}^{\bullet+}$ from perchloro-9,10-dihydrophenanthrene **5**, $C_{15}^{\bullet+}$ perchloro-4,5-methanophenanthrene **6**, $C_{16}^{\bullet+}$ from perchloropyrene **7**, $C_{17}^{\bullet+}$ from perchloro-2,3-benzofluorene **8**, $C_{18}^{\bullet+}$ from perchloro-3,4-benzophenanthrene **9**, and $C_{20}^{\bullet+}$ from perchloroperylene **10**. The results are presented in Table II. Additional preliminary experiments have also been performed with some other perchlorohydrocarbons expected to yield $C_n^{\bullet+}$ with $n = 10$–20.[17] However, in some cases perchlorination of the hydrocarbon was not possible without degradation; in other cases the yield of $C_n^{\bullet+}$ by electron impact induced fragmentation was too low for kinetic experiments.

Scheme I. Reactions of Carbon Cluster Ions $C_n^{\bullet+}$

$$C_n^+ + M \rightleftharpoons [C_n^+ + M]^* \qquad (1)$$

formation of collision complex

$$[C_n^+ + M]^* \rightarrow C_nM^+ + h\nu \qquad (2)$$
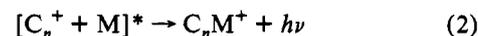
radiative stabilization (direct association)

$$[C_n^+ + M]^* \xrightarrow{M} C_nM^+ \qquad (3)$$
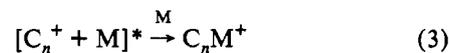
collisional stabilization

$$[C_n^+ + M]^* \rightarrow C_n + M^+ \qquad (4)$$

charge transfer

$$[C_n^+ + M]^* \rightarrow D + E^+ \qquad (5)$$
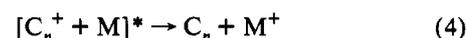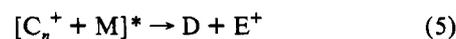
chemical reaction

The ion/molecule reactions of $C_n^{\bullet+}$ observed generally with organic substrates are shown in Scheme I. The excited collision complex $[C_n^{\bullet+} + M]^*$ formed from $C_n^{\bullet+}$ and a neutral molecule M may dissociate back to reactants (back reaction of (1)), may be stabilized by infrared photon emission (2),[25] or may be stabilized by collision with a third body M (3). Radiative association (2) is particularly abundant for carbon cluster ions with $n > 9$.[11,13] Finally, ions $C_n^{\bullet+}$ undergo a charge-transfer reaction with the reactant (4) or form products by an exothermic chemical reaction (5). Which of these reactions occurs depends on the properties of the cluster ions and the neutral reactants, but usually the rate of an exothermic charge transfer exceeds those of other chemical reactions by far, so that the latter one cannot compete. Due to

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the high ionization energy of ACN (IE(ACN) = 10.91 eV[26]) a charge transfer from $C_n^{\cdot+}$ (n = 10–20, IE < 9.1 eV[12a]) is strongly endothermic and is not observed if the ions $C_n^{\cdot+}$ are prepared carefully avoiding any excess kinetic energy. A kinetic energy effect on charge-transfer reactions of $C_n^{\cdot+}$ was also observed by McElvany et al.[11] and Zimmermann et al.[13] but was avoided in our experiments by the procedure described in the Experimental Section.

The reactions of $C_n^{\cdot+}$ with ACN are rather slow with rate constants ranging from <10^{-13} cm^3 molecule^{-1} s^{-1} for $C_{18}^{\cdot+}$ and $C_{20}^{\cdot+}$ to 7.1 × 10^{-10} cm^3 molecule^{-1} s^{-1} for $C_{13}^{\cdot+}$. A low reactivity of $C_n^{\cdot+}$ (n = 10–20) was observed before and was attributed to the cyclic structure of these cluster ions.[11b,c] However, the rate constants of the reactions with HCN[11c] are almost two orders of magnitudes smaller than those of the reaction with ACN, and the faster reactions with ACN allowed the determination of the rate constants for all $C_n^{\cdot+}$ studied. An alternation of the reactivity between odd- and even-numbered $C_n^{\cdot+}$ stated by the empirical rule[11c] is definitely not observed, but $C_{13}^{\cdot+}$ and $C_{17}^{\cdot+}$ exhibit increased reactivity toward ACN. An increased reactivity of $C_{13}^{\cdot+}$ toward HCN was found before.[11c] $C_{13}^{\cdot+}$ exhibits also an increased reactivity toward C_2H_2 and C_2H_4,[11b] but again the reaction of $C_{13}^{\cdot+}$ with ACN is faster by a factor of 33 and 10, respectively, and no reaction of $C_{17}^{\cdot+}$ was reported. In contrast to $C_{13}^{\cdot+}$ and $C_{17}^{\cdot+}$, the rate constants of the reaction of $C_{10}^{\cdot+}$ with C_2H_2 and C_2H_4 exceed that of the reaction with ACN. This comparison shows clearly that at least for cluster ions $C_n^{\cdot+}$ with 10 < n < 20 the reactivity pattern is not determined generally by the "empirical rule" relying on the number of C atoms of the cluster ions but at least as much by other factors, for example, the nature of the reactant. In addition, the thermodynamic stability of the cluster $C_n^{\cdot+}$ also has a distinct effect on the reactivity.[9e] A careful study of the binding energy in $C_n^{\cdot+}$ reveals[27] clear differences for the individual cluster ions and shows that $C_{13}^{\cdot+}$ is the most unstable cluster ion in this series, in agreement with its large reactivity. Another factor appears to be the IE of the carbon cluster which is exceptionally low for the most reactive C_{13} and C_{17}.

There is a possibility that the different reactivities of the cluster ions observed in this and in earlier studies[11] arise from different structures of ions $C_n^{\cdot+}$ generated by different techniques. In particular, a $C_{13}^{\cdot+}$ cluster retaining the structure of the carbon skeleton of the fluorene **4** may be expected to exhibit a large reactivity owing to a carbene center at C-13. Similar special structures can be visualized for the other clusters derived from perchlorinated hydrocarbons. However, this interpretation is not very likely. It is known[8,9,11] that the structure of $C_n^{\cdot+}$ changes from linear to cyclic between n = 9 and n = 11 and that a monocyclic structure is the most stable one for n = 10–20. In line with earlier studies, our AM1 calculations indicate that a $C_{13}^{\cdot+}$ with a fluorene skeleton is unstable. Interestingly, these calculations show that there is another stable structure of $C_{13}^{\cdot+}$ containing the tricyclic carbon skeleton of phenalene, a naphthalene derivative bridged in the 1,8-positions by a C_3 unit. This $C_{13}^{\cdot+}$ isomer has a distinctly larger heat of formation than the monocyclic one, however. Similarly, according to the AM1 calculation an ion $C_{16}^{\cdot+}$ with the carbon skeleton of pyrene is a stable species but much higher in energy than the monocyclic cluster isomer. At least the formation of a phenalene-like $C_{13}^{\cdot+}$ from **4** requires an extensive rearrangement of the carbon skeleton

similar to the formation of the more stable monocyclic isomer and is not very likely. Further, the reactions of the cluster ions with ACN are strictly pseudo-first-order without any indication of the presence of isomers of different reactivity. Finally, the unimolecular dissociations of cluster ions prepared by electron impact induced fragmentation show also no sign of isomers and no differences compared to cluster ions prepared by laser evaporation of graphite.[6,28] Thus, most likely the carbon skeleton of the ionized PPA rearranges during the losses of Cl to the most stable carbon cluster ion, and ions of identical structure were investigated in the various studies.

Adduct formation yielding $C_{n+3}H_3N^{\cdot+}$ is the only reaction with ACN observed for $C_n^{\cdot+}$ with n = 10–20 with the exception of $C_{16}^{\cdot+}$. In this latter case adduct formation is followed by loss of a neutral C_3. The transfer of H atoms to $C_n^{\cdot+}$ occurring with HCN[11c] and hydrocarbons[11b] as reactants at least for the smaller cluster ions is not observed. The mechanism of adduct formation was not studied specifically, but a dependence of the association reaction constant on the reactant pressure in the range used (1.4 × 10^{-8}–14 × 10^{-8} mbar) was not observed. Hence, formation of $C_{n+3}H_3N^{\cdot+}$ occurs very likely by radiative association. Association reactions of $C_n^{\cdot+}$ (n = 10–25) with aromatic hydrocarbons have been observed before by Zimmermann and Creasy,[13] and their work[13b] demonstrated the extreme long lifetime (28–56 ms) of the reactive collision complex [$C_n^{\cdot+}$ + $C_{10}H_8$]* (n = 10–20) owing to the large number of modes, by which the internal energy of the excited complex can be distributed.

In the case of $C_n^{\cdot+}$ with n = 11, 12, and 14 the association of ACN is slow with efficiencies below 3%. Generally, a decrease of the reactivity with the size of the cluster ion is observed, and the efficiency of the reaction of the $C_n^{\cdot+}$, n = 15, 16, 18, and 20, with ACN is below 1%. Thus, these reactions were difficult to follow to near completion due to the small rates, and the rate constants for the reactions of $C_{18}^{\cdot+}$ and $C_{20}^{\cdot+}$ were not determined explicitly. However, $C_{13}^{\cdot+}$ exhibits a rather high reactivity (efficiency 24.3%) toward ACN followed by $C_{10}^{\cdot+}$ (efficiency 9.2%) and $C_{17}^{\cdot+}$ (efficiency 7.0%). Interestingly, both $C_{13}^{\cdot+}$ and $C_{16}^{\cdot+}$ generate product ions $C_{16}H_3N^{\cdot+}$ with ACN, the latter cluster ions by elimination of C_3. Obviously, the association of ACN to $C_{16}^{\cdot+}$ generates a chemically activated species [$C_{19}H_3N^{\cdot+}$]* decomposing either by back dissociation or by loss of C_3. This latter fragmentation may indicate an extra stability of the product ion $C_{16}H_3N^{\cdot+}$, which would also explain the high rate of the association of ACN (=C_3H_3N) to $C_{13}^{\cdot+}$. The reactions of ions $C_n^{\cdot+}$ with HCN gave rise to apparently simple adducts, because the association is reversed on CID. Probably, the adduct ions are formed by bonding of the ion to the N atom of HCN, reminiscent of the Ritter reaction in solution. A similar association has also been suggested for the addition of ammonia and amines to the fullerene radical cation $C_{60}^{\cdot+}$ and dication C_{60}^{2+}.[28] However, preliminary experiments show that carbon cluster ions studied here are unreactive toward acetonitrile, in conflict with an simple nucleophilic attachement of $C_n^{\cdot+}$ to the N atom of nitriles. Thus, the enhanced reactivity of the carbon cluster ions with ACN indicates very likely a different reaction mechanism and hints to the addition of the radical cation $C_n^{\cdot+}$ to the carbon–carbon double bond of ACN. The loss of C_3 accompanying the attachment of ACN to $C_{16}^{\cdot+}$ indicates also a strong chemical bonding of the ACN to the cluster ions, probably accompanied by rearrangement. $C_{16}^{\cdot+}$ retains formally NH$_3$ by the reaction with ACN suggesting the formation of a basic amino group. To get information about the nature of the ACN adduct ions of $C_n^{\cdot+}$, their fragmentation by CID was studied and the gas-phase acidity of the ions (or the proton affinity of the conjugate bases $C_{n+3}H_2N$) was estimated by a bracketing technique with reference bases.

The main reaction of an electrostatically bonded ("simple") adduct ion under CID is expected to be a dissociation back into

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the components, as observed for the adduct ions of cyclic $C_n^{\bullet+}$ with HCN. In the case of the adduct ions of ACN and $C_n^{\bullet+}$ it was difficult to achieve meaningful CID spectra of the ions $C_{n+3}H_3N^{\bullet+}$. This is partly due to the low efficiencies of the reactions forming the adduct ions, but additionally the kinetically excited ions $C_{n+3}H_3N^{\bullet+}$ generate abundant $C_3H_4N^+$ from ACN, still lingering in the ICR cell even after a pumping time of several seconds. The ion $C_3H_4N^+$ may be formed either by a direct proton transfer from $C_{n+3}H_3N^{\bullet+}$ to ACN or by a charge transfer of kinetically excited ions $C_{n+3}H_3N^{\bullet+}$ to ACN to generate $C_3H_3N^{\bullet+}$ followed by a H abstraction from neutral C_3H_3N by this ion. As is shown below, the adduct ions $C_{n+3}H_3N^{\bullet+}$ are rather acidic, making the former mechanism of the formation of $C_3H_4N^+$ more likely.

No fragmentations were observed in the CID spectra of ions $C_{n+3}H_3N^{\bullet+}$ with $n = 11$, 12, and 14, but this may be due to the rather intense loss of parent ions by the formation of $C_3H_4N^+$. CID spectra without too much interference by this ion were achieved only for ions $C_{13}H_3N^{\bullet+}$, $C_{16}H_3N^{\bullet+}$, and $C_{20}H_3N^{\bullet+}$ generated from $C_{10}^{\bullet+}$, $C_{13}^{\bullet+}$, and $C_{17}^{\bullet+}$, respectively. Besides a signal for the ion $C_3H_4N^+$ the CID spectra of $C_{13}H_3N^{\bullet+}$ and $C_{20}H_3N^{\bullet+}$ show dissociation into the original components $C_{10}^{\bullet+}$ or $C_{17}^{\bullet+}$ and C_3H_3N. In contrast, the CID spectrum of $C_{16}H_3N^{\bullet+}$ exhibits only a signal of fragment ions formed by loss of neutral C_3. Thus, the adduct ions $C_{n+3}H_3N^{\bullet+}$ with $n = 10$, 17, and 13 belong apparently to different structural categories. It has been shown by experiment and theory that a loss of C_3 is thermodynamically favored during CID[11a] and photodissociation[29] as well as for metastable decomposition routes[30] of $C_n^{\bullet+}$. It is significant that neither the loss of CN or HCN nor the loss of any other fragment containing the N atom is observed by the CID experiment. This demonstrates clearly strong chemical bonding of the associated ACN molecule to the cluster ions $C_{13}^{\bullet+}$ and point to a special reaction mechanism. It would be of interest to compare this with the CID of $C_{16}H_3N^{\bullet+}$ ions derived from $C_{16}^{\bullet+}$, but the low abundance of the latter ions precluded this experiment.

For examining the gas-phase acidity of the product ions $C_{13}H_3N^{\bullet+}$ and $C_{16}H_3N^{\bullet+}$ generated by ion/molecule reaction with ACN, these ions were isolated and were allowed in a "tandem-ion/molecule" experiment to react with NH_3 (PA = 871.5 kJ/mol[31]), acetone (PA = 830 kJ/mol[31]), isobutene (PA = 820 kJ/mol[26,31]), isobutyronitrile (PA = 813 kJ/mol[26]), 1,4-dioxane (PA = 811 kJ/mol[26]), and propene (PA = 750 kJ/mol[31]) in separate experiments. After a sufficient amount of the product ions was formed by the ion/molecule reaction of $C_n^{\bullet+}$ with ACN, the reference base was introduced into the ICR cell by a pulsed valve. After introducing NH_3, a fast and complete decay of the ions $C_{13}H_3N^{\bullet+}$ or $C_{16}H_3N^{\bullet+}$ and a rapid formation of ions NH_4^+ was observed, very likely by a direct proton transfer from $C_{13}H_3N^{\bullet+}$ or $C_{16}H_3N^{\bullet+}$ to NH_3. A fast charge-transfer reaction between the ions $C_{n+3}H_3N^{\bullet+}$ and NH_3 (10.16 eV) generating $NH_3^{\bullet+}$ and subsequently NH_4^{+} [21] is not expected because of the large IE differences. A proton-transfer reaction was found also from $C_{16}H_3N^{\bullet+}$ to acetone but not to isobutene and propene. Thus, the proton affinity of the conjugate base $C_{16}H_2N$ is bracketed to 825 ± 5 kJ/mol. In the case of ions $C_{13}H_3N^{\bullet+}$, a fast proton transfer was observed to acetone and also to isobutene but not to isobutyronitrile and 1,4-dioxane. This brackets the PA of the conjugate base $C_{13}H_2N$ to 816 ± 4 kJ/mol. These results show that the gas-phase acidity of the two ions $C_{n+3}H_3N^{\bullet+}$ studied is

rather large, and the PA of their respective conjugated bases $C_{n+3}H_2N$ is small.

The small PA of the conjugate bases of the product ions excludes the formation of a protonated amino group, an ionized amine, and a protonated N-heteroaromatic moiety by the incorporation of ACN into the carbon cluster ions, because a much higher PA is associated with these structural elements (aniline, PA = 899 kJ/mol;[31] phenylaminyl radical, PA = 927;[32] pyridine, PA = 952 kJ/mol[31]). However, nitriles (CH_3CH_2CN, PA = 806 kJ/mol;[26,31] C_6H_5CN, PA = 820 kJ/mol[26]) exhibit similar PA, and ACN (PA = 793 kJ/mol[31]) is only slightly less basic than the conjugated bases of the ions $C_{n+3}H_3N^{\bullet+}$ explaining the difficulties during the CID experiments due to the competing proton transfer to ACN. A possible pathway to an ionized nitrile would be a 1,2-addition of the $C_n^{\bullet+}$ to the C–C double bond of ACN, in agreement with the back dissociation of product ions $C_{13}H_3N^{\bullet+}$ and $C_{20}H_3N^{\bullet+}$. However, the presence of a –CN group or a –CN^+H group in the product ions $C_{n+3}H_3N^{\bullet+}$, i.e., an ionized nitrile $C_{n+2}H_3CN^{\bullet+}$ or its distonic isomer $C_{n+2}H_2^{\bullet}CNH^+$, remains doubtful, because one would expect extensive losses of CN and HCN in the CID spectra for these ions, which are not observed. The conjugate base $C_{n+3}H_2N^{\bullet}$ of the product ion corresponds to a radical, and the PA of vinylic carbon radicals (cyclopropenyl radical, PA = 760 kJ/mol; cyclopentadienyl radical, PA 754 kJ/mol;[33] cycloheptadienyl radical PA = 837 kJ/mol;[33] benzyl radical, PA = 833 kJ/mol[32]) are also in the range of 750–840 kJ/mol, while the PA of C_{60} (PA *c.* 860 ± 7 kJ/mol)[34] is again larger. Therefore, structures of the product ions with the N atoms incorporated into a ring and resembling the molecular ions of N-heterocyclic compounds (with a tertiary N) are likely at least for $C_{16}H_3N^{\bullet+}$. One possible mode to generate such cyclic ions $C_{n+3}H_3N^{\bullet+}$ would be a 1,4-addition of $C_n^{\bullet+}$ to ACN followed by ring expansion to a larger cyclic ring structure. However, the experimental information available is still too scanty to deduce a detailed structure of the product ions $C_{n+3}H_3N^{\bullet+}$.

The mechanism of a reaction of the individual clusters $C_n^{\bullet+}$ with ACN may be in fact different. It should be remembered that the carbon cluster ions $C_n^{\bullet+}$ correspond to unsaturated radical cations, and the reaction mechanism of these species with electron rich organic reagents is not very well understood.[35] Very likely the energy and the shape of the HOMO of the respective cluster ion play a decisive role, and the mechanism should be analyzed by the configuration mixing model of Shaik and Pross.[36] We have shown recently that the gas-phase reactions of the radical cations of aromatic hydrocarbons[37] can be analyzed by the model and that the differences of the IE of the reactants can be critical for the reactivity. In this connection it is of interest to note that the IE of the clusters C_n, $n = 10$–20, varies considerably[9e,12a] and that the clusters C_{13} and C_{17} are exceptional because of a low IE. These two cluster ions exhibit a high reactivity toward ACN, stressing the decisive role of the IE for the reactions of radical cations. In addition, AM1 calculations reveal distinct and nonsystematic differences between the total spin density of the HOMO of the individual cluster ions $C_n^{\bullet+}$. Thus it appears that the cluster ions $C_n^{\bullet+}$ with $n = 10$–20 do not present a uniform class of compounds with a typical reactivity but have to be taken individually. The present results concerning the reactions of $C_n^{\bullet+}$ with ACN as well as the results of a study of other reactions of

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these cluster ions to be discussed in forthcoming papers support the impression of rather a specific reactivity of the individual carbon cluster ion than a general group reactivity toward organic substrates for medium size carbon cluster ions.

Conclusion

The ion/molecule reactions of the carbon clusters studied so far allow the following general conclusions: (1) the carbon cluster ions $C_n^{\bullet+}$ ($n = 10$–18 and 20) exhibit a distinct reactivity toward acrylonitrile exceeding in most cases that observed with C_2H_4 and in particular with HCN. (2) The periodic alternation of the reactivity of odd- and even-numbered carbon cluster ions is not observed for the reaction with acrylonitrile. (3) No isomers of a certain cluster ion $C_n^{\bullet+}$ have been detected so far by the observation of bimodal reaction kinetics. (4) $C_{13}^{\bullet+}$ and $C_{17}^{\bullet+}$ exhibit an extraordinary reactivity toward ACN, and the reactivity pattern with this substrate depends clearly not only on the size and odd or even carbon atom number of the cluster ion but also on the nature of the reactant, on the stability of the cluster ion,

and on the IE of the neutral carbon cluster. (5) The CID experiments with ions $C_{16}H_3N^{\bullet+}$ have revealed strong chemical bonding between the carbon cluster ion $C_{13}^{\bullet+}$ and ACN, and this is likely true also for some of the adducts of ACN with the other cluster ions. However, the product ion $C_{13}H_3N^{\bullet+}$ dissociates back on CID. (6) The proton affinities of the conjugate bases $C_{n+3}H_2N^{\bullet}$ of the product ions are between 810–825 kJ/mol, which is not compatible with the presence of a protonated amino group or N-heteroaromatic group in these product ions but would agree with the structure of an ionized nitrile or a polycyclic unsaturated hydrocarbon.