Isomeric $C_{24}^{\bullet+}$ Carbon Cluster Ions Derived from Perchlorocoronene. Reactions of Carbon-Cluster Ions with Pyridine

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Carbon cluster ions $C_{24}^{\bullet+}$ have been generated from dodecachlorocoronene $C_{24}Cl_{12}$ by electron-impact ionization followed by *collision-induced dissociation* (CID) of the molecular ions $C_{24}Cl_{12}^{\bullet+}$ and fragment ions $C_{24}Cl_x^{+}$ using the technique of *multiple-excitation collisional activation* (MECA) and Fourier transform ion-cyclotron resonance spectrometry. The ions $C_{24}^{\bullet+}$ were reacted with several organic reactants, but a fast reaction was observed only with pyridine, resulting in the addition of pyridine molecules. One fraction of the $C_{24}^{\bullet+}$ cluster ions adds only a single pyridine molecule, and the adduct ion dissociates back to the starting material on CID. The remaining fraction adds up to five molecules of pyridine. CID of the product ion formed by addition of three pyridines shows that from this adduct ion none of the pyridine molecules is lost. It is suggested that the formation of two isomeric $[C_{24}; \text{pyridine}]^{+-}$ adduct ions is due to the presence of two isomeric $C_{24}^{\bullet+}$ ions generated by MECA from $C_{24}Cl_{12}^{\bullet+}$ ions and fragment ions $C_{24}Cl_x^{+}$. For a comparison the reactions of $C_n^{\bullet+}$, $n = 12-14$, with pyridine were investigated. These smaller carbon cluster ions were generated from appropriate perchloroarenes by exhaustive dechlorination by electron-impact ionization and are known to exist exclusively as monocyclic carbon rings. The reaction of these monocyclic $C_n^{\bullet+}$ with pyridine proceeds also by addition of two or three pyridine molecules. Therefore, it is concluded that the $C_{24}^{\bullet+}$ isomer, which reacts by multiple pyridine attachment, corresponds to an isomer with a monocyclic structure, in line with recent data from the literature. For the second $C_{24}^{\bullet+}$ isomer a graphitic structure with the carbon skeleton of coronene is suggested. This $C_{24}^{\bullet+}$ isomer undergoes fast reaction but adds only one pyridine molecule.

Introduction

The reactions of ionized carbon cluster ions $C_n^{\bullet+}$ continue to be of interest because of the importance of carbon clusters both for the chemistry of flames and related industrial processes and for interstellar chemistry.[1] Much of the work has been focused on the reactions of small carbon cluster ions $C_n^{\bullet+}$, $n < 10$, which display high carbenic reactivity,[2] and of ionized C_{60} and higher fullerene ions, which exhibit a rich chemistry as multiply charged ions.[3] Carbon cluster ions containing 10−20 carbon atoms are distinguished from the smaller clusters and the fullerenes by a distinct reactivity only toward certain unsaturated compounds such as α,β-unsaturated nitriles,[4] haloalkenes,[5] and arenes.[6] In all these reactions the cluster ions of this size exhibit a reactivity alternating with $n = 4p + 1$ and $n = 4p + 3$ indicating "aromatic" and "antiaromatic" electronic configurations of the cluster ions. Additionally, these $C_n^{\bullet+}$ yield different product ions for clusters containing an odd or even number of carbon atoms. The different reactivity of the $C_n^{\bullet+}$ of various size can be correlated with different structures of the carbon clusters. It is known from ion-mobility measurements[7] that $C_n^{\bullet+}$, $n < 10$, are linear, that $C_n^{\bullet+}$, $n = 10-20$, have a monocyclic structure, and that $C_n^{\bullet+}$ with $n > 20$ exhibit other structures, possibly polycycles, besides monocyclic rings. The spherical structure of the fullerenes is first observed for cluster ions around $C_{30}^{\bullet+}$ and starts to dominate for $C_n^{\bullet+}$, $n > 30$. For carbon cluster ions $C_n^{\bullet+}$, $n = 20-40$, polycyclic structures compete in stability with monocyclic structures and mixtures of isomers are created by laser evaporation of graphite as shown by ion-mobility measurements.[7] However, the ion/molecule reactions of carbon cluster ions of this size have rarely been studied specifically. The gross reactivity of $C_n^{\bullet+}$ tends to decrease with cluster size; hence, it is difficult to find suitable reaction partners for cluster ions of this size to probe a structure/reactivity relationship.

Recently, Lifshitz et al.[8] have shown that $C_n^{\bullet+}$ of selected size can be prepared conveniently by electron-impact-induced dissociation of perchlorinated organic compounds, preferentially perchloroarenes, and we have used this method to prepare $C_n^{\bullet+}$, $n = 10-20$, and to study their ion/molecule reactions by Fourier transform ion-cyclotron resonance (FT-ICR) spectrometry.[4,5,6d] Perchloroarenes are readily accessible by perchlorination of the respective arenes according to Ballester et al.[9] However, the relative amount of $C_n^{\bullet+}$ generated by electron-impact-induced dissociation of the perchloroarene decreases distinctly with the molecular size, since the energy necessary for an increasing number of multiple fragmentations has to be imparted to the parent ion during the ionization event. Therefore, the generation of $C_n^{\bullet+}$ with $n > 20$ with an abundance sufficient for kinetic studies by FT-ICR proved to be impossible by this simple technique.

The fragmentation of gaseous ions can also be achieved by collisional activation (CA) during the collisions of fast-moving ions with neutral atoms or molecules. A collision-induced dissociation (CID) of a large ion can be performed by FT-ICR by accelerating the ion by an rf impulse with the appropriate

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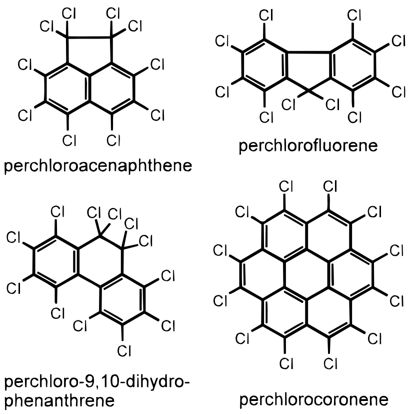
SCHEME 1



cyclotron frequency and introducing argon as a collision gas into the FT-ICR cell.[10] A single collision (or even a few collisions) of the molecular ion of a perchloroarene with argon does not deliver enough excess energy for a complete dechlorination by loss of 12 or more Cl substituents. However, the product ions of CID can be stored in the FT-ICR cell and may undergo further CID if kinetically excited again. Thus, the chloro substituents may be eliminated step by step, and eventually, the carbon skeleton may form the corresponding carbon cluster ion $C_n^{\bullet+}$. With the advent of the modern CA techniques of FT-ICR spectrometry described as MECA (multiply excited CA)[11] and SORI (sustained off-resonance irradiation),[12] it also appeared possible to generate in this way specifically $C_n^{\bullet+}$ with $n > 20$ from appropriate perchloroarenes. In this paper we report the successful application of the MECA technique to the generation of $C_{24}^{\bullet+}$ from dodecachlorocoronene $C_{24}Cl_{12}$. The ion/molecule reactions of this carbon cluster ion have been studied, in particular with pyridine, and have been compared with the reactions of monocyclic $C_{12}^{\bullet+}$, $C_{13}^{\bullet+}$, and $C_{14}^{\bullet+}$. It will be shown that the $C_{24}^{\bullet+}$ generated in this way by MECA from ionized dodecachlorocoronene differ in their reactivity from $C_{24}^{\bullet+}$ produced by laser evaporation and probably consist of two isomers that are distinguished by their reaction products with pyridine.

Experimental Section

Pure pyridine (>99%) and the other neutral reagents used in this work are commercially available and were used without further purification. Perchloroacenaphtene $C_{12}Cl_{10}$, perchlorofluorene $C_{13}Cl_{10}$, and perchloro-9,10-dihydrophenanthrene $C_{14}Cl_{12}$ (for structures see Scheme 1) were available from our earlier work.[4,5] Perchlorocoronene $C_{24}Cl_{12}$ (Scheme 1) was prepared as described before[4a] according to the method of Ballester et al.[9] by heating 10 mmol coronene with the so-called 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 to 70 °C for several hours and controlling the reaction by thin-layer chromatography. Following the usual workup[4a] the perchloroarenes were purified by column chromatography on silica gel. The structure of $C_{24}Cl_{12}$ was confirmed by the 70-eV mass spectrum and the ^{13}C NMR spectrum.

The ion/molecule reactions of the carbon clusters $C_n^{\bullet+}$ were studied as described before[3] using a Bruker CMS 47X FT-ICR spectrometer equipped with an external ion source and an Infinity cell. Different techniques were used to prepare the cluster ions $C_n^{\bullet+}$, $n = 12-14$, and $C_{24}^{\bullet+}$. The smaller cluster ions can be generated with sufficient intensity directly from the respective perchloroarene by electron-impact-induced dissociation using 30-eV electrons. As described in previous papers,[4,5] the ion mixture produced by electron-impact ionization was transferred into the FT-ICR cell and the $C_n^{\bullet+}$ were isolated by ejection of all other ions by the FERETS technique, which is a computer-controlled combination of a broad-band ejection and single rf pulses at selected frequencies. Following this procedure, the ions $C_n^{\bullet+}$ were thermalized by collision with argon gas admitted into the ICR cell by a pulsed valve. Then a variable delay time was used to permit ion/molecule reactions to occur with a neutral reactant present in the FT-ICR cell at a constant background pressure of $(1-20) \times 10^{-8}$ mbar.

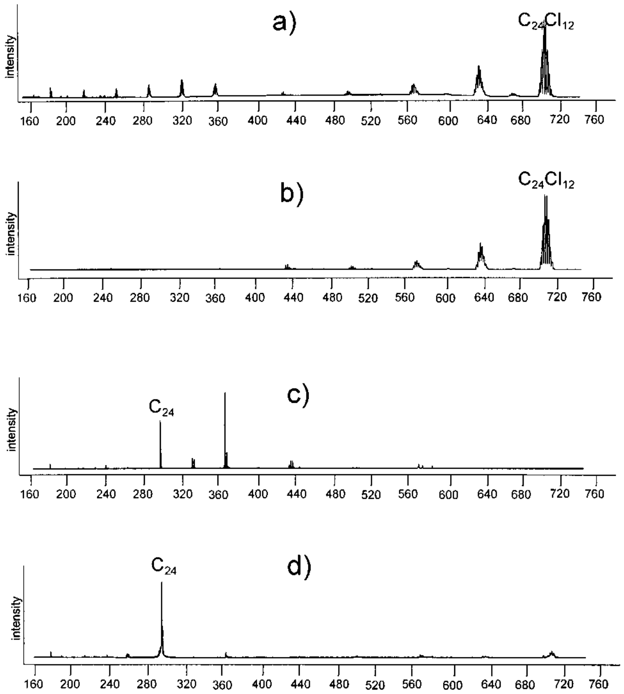


Figure 1. Preparation of $C_{24}^{\bullet+}$ from $C_{24}Cl_{12}^{\bullet+}$ by MECA: (a) 30-eV EI-mass spectrum of $C_{24}Cl_{12}$; (b) mass spectrum after ejection of all ions below *m/z* 365; (c) mass spectrum after 45 MECA cycles; (d) mass spectrum after 70 MECA cycles.

The relative intensity of fragment ion $C_{24}^{\bullet+}$ in the electron-impact mass spectrum of $C_{24}Cl_{12}$ is below 1% and too small for kinetic experiments. Hence, the $C_{24}^{\bullet+}$ ions were generated from all $C_{24}Cl_x^+$ ions ($x = 0-12$) in the EI mass spectrum of $C_{24}Cl_{12}$ by CID of these ions in the FT-ICR cell using the MECA technique.[11] The MECA procedure used followed closely the original protocol given by S. A. Lee et al.[11] First, all ions generated from $C_{24}Cl_{12}$ in the ion source were transferred to the ion cell (see mass spectrum in Figure 1a) and all multiply charged ions below *m/z* 365 were eliminated from the cell by a broad-band ejection to give the mass spectrum of the remaining $C_{24}Cl_x^+$ ions shown in Figure 1b. Argon gas was present in the FT-ICR cell at a constant background pressure of $(5-10) \times 10^{-8}$ mbar and was admitted additionally into the FT-ICR cell by a pulsed valve as a pressure pulse for 3 ms, raising the argon pressure to ca. 10^{-5} mbar. All $C_{24}Cl_x^+$ ions were accelerated by a low-amplitude sweep excitation (sweep rate of ca. 10 Hz/μs) exciting the ions typically up to 20 eV. The excited ions were allowed to relax by collision with argon for 100 μs, and the whole procedure was repeated 45 times before data acquisition. As can be seen from the mass spectrum Figure 1c, most of the $C_{24}Cl_x^+$ ions containing more than two Cl atoms have disappeared after these 45 pulses, and the relative intensity the carbon cluster ion $C_{24}^{\bullet+}$ has increased very much. Continuing MECA by an additional series of 25 rf pulses in the same manner as before results in the mass spectrum in Figure

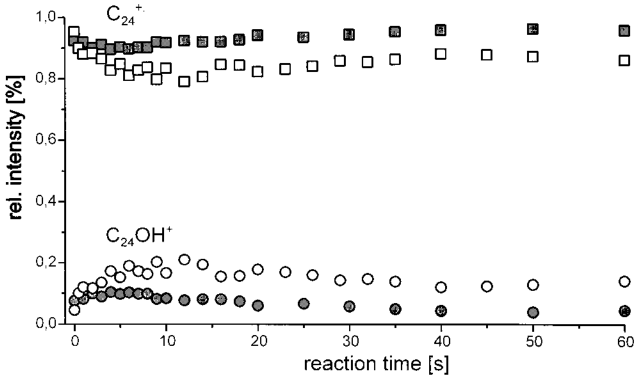


Figure 2. Kinetic plot for the reaction of carbon cluster ions $C_{24}^{\bullet+}$ with ethanol: (filled symbols) pressure of EtOH = 0.9×10^{-7} mbar; (open symbols) pressure of EtOH = 6.0×10^{-7} mbar.

1d, showing only carbon cluster ions $C_{24}^{\bullet+}$ as abundant ions. It is estimated that about 50% of all $C_{24}Cl_x^{+}$ ions originally present in the ICR cell are converted into $C_{24}^{\bullet+}$ by this procedure. Finally, the $C_{24}^{\bullet+}$ ions were again mass-selected by FERETS, thermalized by collision with argon gas as usual,[4a] and allowed to react with the neutral reactant present in the ICR cell at a constant background pressure of about 10^{-8} mbar.

The pressure within the FT-ICR cell was measured by an ionization gauge close to the high-vacuum pump of the FT-ICR cell. The pressure reading was calibrated by rate measurements of the reactions $CH_4^{\bullet+} + CH_4$ and $NH_3^{\bullet+} + NH_3$ as described before[4,5] and corrected by the sensitivity constant of the respective reactant by standard method.[13]

The experimental rate constant k_{exp} of the ion/molecule reactions was determined from the decay of the $C_n^{\bullet+}$ with time ("kinetic plot") by curve-fitting using the Origin PC program.[14] Then k_{exp} was converted into the bimolecular rate constant k_{bi} by taking into account the number density of the neutral reactant in the ICR cell derived from the reactant gas pressure at a temperature of 300 K. The reaction efficiency eff = 100 (k_{bi}/k_c)[%] was obtained from the ratio of the experimental k_{bi} and the theoretical collision constant k_c, which was calculated according to the method of Su and Chesnavich.[15] The reproducibility of k_{exp} is better than 10%, but the main error of the absolute value of k_{bi} is about 25% due to the error in the measurement of the partial pressure of the neutral reactant.

Results and Discussion

Reactions of $C_{24}^{\bullet+}$. In test reactions with ammonia, methylamine, methane, isobutene, crotonitrile, 2-chloropropene, benzene, anisole, and aniline, the carbon cluster ions $C_{24}^{\bullet+}$ turned out to be unreactive. Smaller carbon cluster ions are known to form product ions with these reagents, but the rate constants decrease considerably with the cluster size.[2-6] A slow reaction of $C_{24}^{\bullet+}$ was observed with methanol and ethanol, yielding $C_{24}OH^{+}$ during the initial stages of the reaction (Figure 2). But after about 10% conversion, the reaction stopped and the product ions $C_{24}OH^{+}$ disappeared, apparently regenerating $C_{24}^{\bullet+}$ by reaction with the neutral alcohol. No explanation can be given for this surprising observation, but it may be connected with the existence of isomeric $C_{24}^{\bullet+}$.

In contrast to the unreactivity of $C_{24}^{\bullet+}$ toward most other reactants, a fast reaction of $C_{24}^{\bullet+}$ with pyridine was observed. A kinetic plot of this reaction is shown in Figure 3. Under the conditions used no remaining cluster ions $C_{24}^{\bullet+}$ are detected after 6 s and excellent pseudo-first-order kinetics for the disappearance of $C_{24}^{\bullet+}$ are revealed by a semilog plot of the intensity data (see inset in Figure 3). The rate constant k_{bi} = (1.57 ± 0.3) × 10^{-9} [molecules cm^{-1} s^{-1}] is obtained from these data, which corresponds to a reaction efficiency eff = 95%. Thus, the reaction of $C_{24}^{\bullet+}$ created from $C_{24}Cl_{12}^{\bullet+}$ and its fragment ions by MECA with pyridine is controlled by the collision rate.

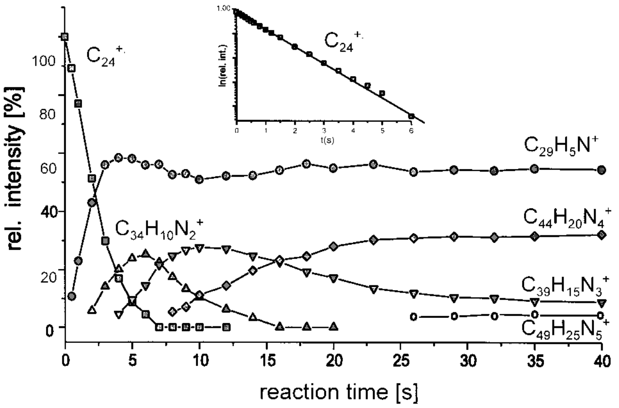


Figure 3. Kinetic plot for the reaction of carbon cluster ions $C_{24}^{\bullet+}$ with pyridine: (background pressure *p*) *p*(Ar) = 8.4×10^{-8} mbar and *p*(pyridine) = 1.4×10^{-8} mbar). The insert presents a semilog plot of the data for the decay of $C_{24}^{\bullet+}$.

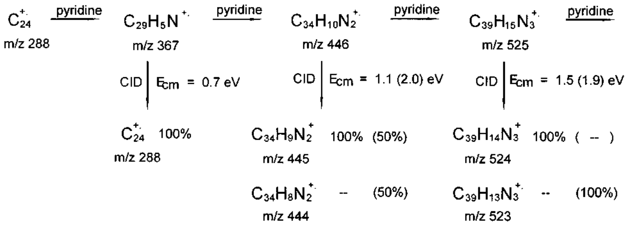
The primary product ion $C_{29}H_5N^{\bullet+}$ corresponds to an adduct ion of $C_{24}^{\bullet+}$ and pyridine. Clearly, two isomeric product ions $C_{29}H_5N^{\bullet+}$ are formed; one product ion is stable toward further reaction with pyridine while the other one adds quickly a second pyridine molecule that generates $C_{34}H_{10}N_2^{\bullet+}$ as a secondary product ion. The intensity of this secondary product ion reaches a maximum at about 5 s of reaction time, and it has disappeared from the reaction mixture after about 16 s by addition of a third molecule of pyridine and producing tertiary ions $C_{39}H_{15}N_3^{\bullet+}$. Again, a fourth molecule of pyridine is added to these $C_{39}H_{15}N_3^{\bullet+}$ ions to yield $C_{44}H_{20}N_4^{\bullet+}$ ions that are the main product ions at 40 s of reaction time besides the unreactive primary ions $C_{29}H_5N^{\bullet+}$. At this stage of the reaction even $C_{49}H_{25}N_5^{\bullet+}$ product ions are observed, generated by the addition of five molecules of pyridine to the original carbon cluster $C_{24}^{\bullet+}$, although the reaction rate is by now very slow. Thus, it was not possible to ascertain whether more than five pyridines can be attached to this cluster ion.

The unreactive and the reactive isomers of $C_{29}H_5N^{\bullet+}$ are obviously generated by independent parallel reactions with $C_{24}^{\bullet+}$ as indicated by a maximum of the ion-yield curve at a reaction time of 4–5 s. There are two explanations possible for this observation. First, the $C_{24}^{\bullet+}$ cluster ions generated by MECA from the perchlorocoronene are a homogeneous population of ions of a single structure, which produces two isomeric $C_{29}H_5N^{\bullet+}$ product ions by reaction with pyridine. This situation has been observed for the reactions of $C_n^{\bullet+}$ cluster ions, which produce $C_{n+3}H_5^{+}$ product ions with chloropropenes[5] by elimination of Cl. In the case of the $C_{13}^{\bullet+}$ and $C_{17}^{\bullet+}$ cluster ions, isomeric $C_{n+3}H_5^{+}$ product ions are formed because a certain fraction of these ions undergo secondary reactions with the chloropropene.[5] The second possibility is the formation of isomeric $C_{24}^{\bullet+}$ cluster ions by MECA from perchloropropene, which then give rise to isomeric primary product ions $C_{29}H_5N^{\bullet+}$. There are some strong indications that this second explanation is in fact the correct one.

The $C_{24}^{\bullet+}$ cluster ions prepared in this work by MECA from perchlorocoronene exhibit an extraordinary reactivity toward pyridine that surpasses that of smaller $C_n^{\bullet+}$ (see below). This is rather atypical because usually the reactivity of $C_n^{\bullet+}$ cluster ions decreases with the number of C atoms. After finishing the experiments and preparing this manuscript, Pozniak and Dunbar published their results of a study of the reactivity patterns of $C_n^{\bullet+}$ cluster ions ($n = 10-24$) with nitrogen-containing molecules including unsaturated nitriles and pyridine.[16] In this study the $C_n^{\bullet+}$ cluster ions were prepared "conventionally" by laser vaporization of graphite, which is known to produce only or at least predominantly monocyclic $C_n^{\bullet+}$ cluster ions.[7] The rate constants for the reactions of C_n^{+} with nitriles obtained by this group and reported by us earlier[4] are in reasonable agreement[17] for $C_n^{\bullet+}$ ($n = 10-20$), showing again[7b] that electron-impact-induced perdechlorination of perchloroarenes in a single high-energy step creates the most stable monocyclic $C_n^{\bullet+}$ cluster ions. In agreement with our results Pozniak and Dunbar observed practically no reaction of $C_{24}^{\bullet+}$ with nitriles but a distinct reaction with pyridine and pyrrole. Unfortunately, the rate constants given by them for the pyridine reaction are too large by nearly 1 order of magnitude, as mentioned by these authors,[16] so that no direct comparison with our values is possible. Nevertheless, it is clear from their *relative* rate constants for the reaction of $C_n^{\bullet+}$ cluster ions with pyridine that the reaction efficiency *decreases* from $C_{11}^{\bullet+}$ and $C_{12}^{\bullet+}$ to $C_{24}^{\bullet+}$ as usual by almost a factor of 4. In contrast, the $C_{24}^{\bullet+}$ prepared here by MECA from perchlorocoronene show an *increase* of the reaction efficiency compared with $C_{12}^{\bullet+}$ prepared by electron-impact-induced dechlorination of perchloroacenaphthene (see below). Thus, it is evident that the $C_{24}^{\bullet+}$ cluster ions generated by MECA and by laser evaporation exhibit different reactivities and must be a result of isomers exhibiting different reactivities. Further, Pozniak and Dunbar observed secondary reactions by "clustering" of the neutral reagent[16] but do not report the outstanding bimodal reaction observed here for the additional reactions of the primary addition product of pyridine to $C_{24}^{\bullet+}$. Obviously, their $C_{24}^{\bullet+}$ cluster ions prepared by laser vaporization are more or less homogeneous. It is still possible that the $C_{24}^{\bullet+}$ isomer obtained in this work by MECA isomerizes to some extent within the collision complex with pyridine into monocyclic $C_{24}^{\bullet+}$ during the reaction because of electrostatic activation by ion/dipole attraction in the complex. However, this is not very likely because this isomer of $C_{24}^{\bullet+}$ has already survived collisional activation by MECA, indicating a rather large activation energy for the isomerization. In this connection it must be noted that the $C_{24}^{\bullet+}$ cluster ions were prepared by MECA of the $C_{24}Cl_{12}$ molecular ions of perchlorocoronene *and of $C_{24}Cl_x$ ($x = 1-11$)* fragment ions obtained by electron impact. It is possible that some of these fragment ions have not only lost Cl substituents but have also rearranged their carbon skeleton. Therefore, we suggest that the $C_{24}^{\bullet+}$ cluster ions obtained in this way are already a mixture of isomers.

Since the experimental rate constant obtained here for the reaction of $C_{24}^{\bullet+}$ cluster ions with pyridine reflects only the collision rate of the mixture of $C_{24}^{\bullet+}$ with pyridine, it is not possible to determine the rate constants for the individual $C_{24}^{\bullet+}$ isomers. We were unable to alter the composition of the ion mixture prepared by MECA by modifying the experimental conditions. With our FT-ICR instrument it turned out to be rather difficult to alter the collision energy of the MECA procedure over a broader range because of inefficient fragmentation of the perchlorocoronene ions at small collision energies or severe ion loss by scattering at large collision energies. In all cases, where a sufficient intensity of $C_{24}^{\bullet+}$ was obtained from ionized dodecachlorocoronene, a 1:1 branching into the isomers had occurred as shown by the 50 ± 10% relative intensity of the unreactive $C_{29}H_5N^{\bullet+}$ observed at the final stage of the total reaction.. However, the constant composition of the $C_{24}^{\bullet+}$ mixture reflects very likely only the instrumental limitations.

SCHEME 2

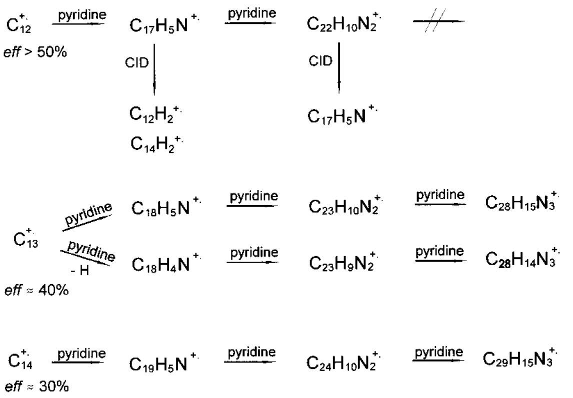


CID of Product Ions [$C_{24}^{\bullet+} + n(C_5H_5N)$]. Information about the structures of the product ions of the reaction of $C_{24}^{\bullet+}$ with pyridine and therefore also about the structure of the isomeric $C_{24}^{\bullet+}$ can be obtained by collision-induced decomposition. Only the unreactive monoadduct ions $C_{29}H_5N^{+\cdot}$, which was isolated at the final stages of the reaction, could be investigated by CID because the other isomer is never present in the mixture in pure form and reacts quickly with the excess pyridine during the isolation procedure without reaching a sufficient concentration. However, it was possible to isolate the adduct ions of two and three molecules of pyridine to $C_{24}^{\bullet+}$, $C_{34}H_{10}N_2^{\bullet+}$, and $C_{39}H_{15}N_3^{\bullet+}$, respectively, by ejection of all other ions at reaction times shortly before the intensity maxima of these ions (5 and 10 s under conditions similar to Figure 3) and to perform CID on these ions without too much loss of intensity by further reaction with pyridine. The results are presented in Scheme 2.

On CID the unreactive isomer of the monoadduct ion $C_{29}H_5N^{\bullet+}$ dissociates back into the starting material, the cluster ion $C_{24}^{\bullet+}$ and pyridine, as the only reaction observed. This may be due to a structure of this $C_{29}H_5N^{\bullet+}$ ion corresponding to a $C_{24}^{\bullet+}$ ion solvated by a pyridine molecule, but more likely the structure corresponds to pyridinium ion generated by nucleophilic attachment of the pyridine N by its lone pair to the electrophilic carbenium center of $C_{24}^{\bullet+}$. In any case these $C_{29}H_5N^{\bullet+}$ product ions retain the C_{24} and the pyridine entity as structural subunits that reappear on CID. This is obviously not the case for the other reactive isomer of the monoadduct ion $C_{29}H_5N^{\bullet+}$. Its additional product ions $C_{34}H_{10}N_2^{\bullet+}$ and $C_{39}H_{15}N_3^{\bullet+}$ generated by addition of a second and a third pyridine molecule do not exhibit loss of pyridine or regeneration of $C_{24}^{\bullet+}$ under similar CID conditions as used before. Instead, the loss of an H atom and, by increasing the collision energy, of two H atoms (or an H_2 molecule) is observed. These fragmentations are typically of molecular ions of polycyclic arenes and related compounds[18] and have also been observed by CID of the product ions of smaller $C_n^{\bullet+}$ with benzene and fluorinated benzenes.[6d] It is clear from these experiments that all two or three pyridine molecules are much stronger bound to the reactant $C_{24}^{\bullet+}$ in the product ions $C_{34}H_{10}N_2^{\bullet+}$ and $C_{39}H_{15}N_3^{\bullet+}$ than in the case of the unreactive $C_{29}H_5N^{\bullet+}$ product ion. Since only losses of H and 2H are observed, it is not possible to decide whether the two or three pyridine molecules are attached separately at different C atoms of $C_{24}^{\bullet+}$ or whether some kind of "chain polymerization" of pyridine has been initiated by $C_{24}^{\bullet+}$. However, very likely the carbon skeletons of the carbon cluster ion and the pyridine molecule have been merged into a completely new structure as suggested for the reactions of $C_n^{\bullet+}$ with benzene and polyfluorobenzenes.[6]

Reactions of $C_n^{\bullet+}$, $n = 12-14$, with Pyridine. It is known that $C_n^{\bullet+}$, $n = 10-20$, exist only in the form of monocyclic rings if they are prepared by electron-impact-induced per-

SCHEME 3



dechlorination[4,5,7b] or laser vaporization of graphite. Hence, an analysis of the reaction of the smaller carbon cluster ions $C_{12}^{\bullet+}$, $C_{13}^{\bullet+}$, and $C_{14}^{\bullet+}$ with pyridine provides information about the behavior of monocyclic carbon cluster ions toward this reagent. The results are summarized in Scheme 3.

The three $C_n^{\bullet+}$, $n = 12-14$, generate adduct ions with pyridine, although the reaction efficiency for these ion/molecule reactions are less than the collision rate. In contrast to the reactions of the $C_n^{\bullet+}$ with other neutrals the "antiaromatic" $C_{13}^{\bullet+}$ is not distinguished from its neighbors by an increased reactivity but appears to exhibit a somewhat reduced reactivity. Nevertheless, the formation of adduct ions is accompanied in the case of $C_{13}^{\bullet+}$ by a hydrogen-loss channel [adduct − H], as usual for $C_n^{\bullet+}$ containing an odd number of carbon atoms.[6] It has been mentioned above that Pozniak and Dunbar also studied the reactions of $C_n^{\bullet+}$, $n = 12-14$ with pyridine[16] but that the absolute rate constants given are not reliable because of instrumental problems. However, the slightly decreased rate constant in this series for $C_{13}^{\bullet+}$ and the formation of [adduct − H] product ions agree with their *relative* rate constants.

Interestingly, for all three monocyclic $C_n^{\bullet+}$ the monoadduct ion reacts quickly by further addition of pyridine molecules, a total of two pyridines in the case of $C_{12}^{\bullet+}$ and three pyridines in the cases of $C_{13}^{\bullet+}$ and $C_{14}^{\bullet+}$. However, for the latter reactions the attachment of a third pyridine molecule was observed only with rather small intensities at long reaction times. Again, the attachment of two and three pyridine molecules ("clustering") to the primary monoadduct ion conforms with the results of Pozniak and Dunbar[16] obtained for $C_n^{\bullet+}$ generated by graphite evaporation. Thus, these results prove that *addition of more than one pyridine molecule occurs typically for the ion/molecule reactions of monocyclic* $C_n^{\bullet+}$.

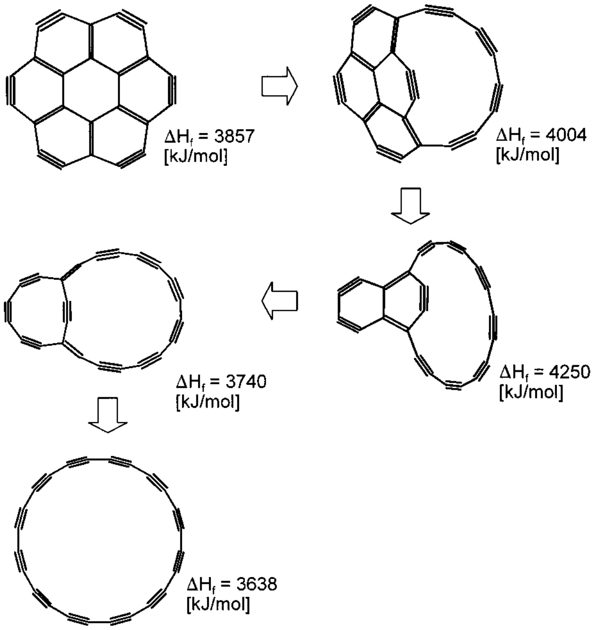
For the reaction products of $C_{12}^{\bullet+}$ with pyridine, only the structure of the adduct ions could be analyzed by CID. The results are included in Scheme 3 and reveal a completely different behavior of the pyridine monoadduct ion of $C_{12}^{\bullet+}$ and the *unreactive* monoadduct ion of $C_{24}^{\bullet+}$. In the latter case only back dissociation into the reactants occurs by CID. In the former case this is not observed at all but dissociation into fragment ions $C_{12}H_2^{\bullet+}$ and $C_{14}H_2^{\bullet+}$ was observed. Analogous fragmentations to $C_nH_2^{\bullet+}$ ions have been observed for the adduct ions produced from $C_n^{\bullet+}$ and fluorobenzenes,[6d] and it was demonstrated for these adduct ions that a reduction of the collision energy switches the CID process to losses of H, H_2, and HF. It is obvious from the CID results that the pyridine moiety is so strongly bonded in the pyridine adduct ion $C_{17}H_5N^{\bullet+}$ of $C_{12}^{\bullet+}$ and so intermingled with the monocyclic carbon cluster that it cannot been released by collisional activation. This is different for the second pyridine molecule attached in the tertiary product ion $C_{22}H_{10}N_2^{\bullet+}$ of $C_{12}^{\bullet+}$. Here, loss of pyridine is the only process observed during CID. Again, an analogous behavior has been observed for the reaction products of $C_n^{\bullet+}$ with fluorinated benzenes.[6d]

Structure of the Isomeric $C_{24}^{\bullet+}$ Ions. Experiment and theory agree that for carbon cluster ions $C_n^{\bullet+}$ with n up to 30 the most stable structure corresponds to a monocyclic ring[7] with two delocalized π-electron systems, the first one built by the cyclic array of parallel carbon 2p orbitals perpendicular to the plane of the ring, the other one by the cyclic array of carbon 2p orbitals (or probably "$2sp^x$" hybrid orbitals) within the plane of the ring. It appears a priori very likely that one of the $C_{24}^{\bullet+}$ isomers generated from the perchlorocoronene $C_{24}Cl_{12}$ by electron-impact ionization and CID with the MECA method corresponds to this most stable structure. It is known from studies of smaller perchloroarenes[4,5,7b] that their molecular ions eliminate all Cl substituents and rearrange into monocyclic $C_n^{\bullet+}$. The reactions of $C_{12}^{\bullet+}$, $C_{13}^{\bullet+}$, and $C_{14}^{\bullet+}$ with pyridine show that these monocyclic carbon cluster ions react with pyridine by addition of more than one pyridine molecule and that at least one of the pyridines added is deeply integrated into the monocyclic carbon ring. The same behavior has been demonstrated for the reactive isomer of the $C_{24}^{\bullet+}$−pyridine adduct ion. Finally, the reactive isomer of $C_{24}^{\bullet+}$ behaves very similarly to the $C_{24}^{\bullet+}$ cluster ion generated by Pozniak and Dunbar by laser vaporization of graphite.[16] The only difference is the addition of at least five pyridine molecules, while Pozniak and Dunbar observed a maximum of only three pyridine molecules attached to $C_{24}^{\bullet+}$. This may be due to small differences of the excess kinetic energy of the ions within both FT-ICR cells.[17]

The structure of the $C_n^{\bullet+}$−pyridine adduct ions is not known, but it is reasonable to assume that the addition proceeds by cycloaddition or ring coalescence between $C_n^{\bullet+}$ and the aromatic ring of the neutral partner followed by rearrangements as suggested for the addition of crotonitrile and chloropropenes to monocyclic $C_n^{\bullet+}$.[4b,5] A similar sequence of events during the ion/molecule reactions of medium-sized $C_n^{\bullet+}$ has also been suggested by N. S. Goroff as the main route to fullerene formation.[19] In this connection it should be remembered that cycloaddition reactions are extremely accelerated by converting one of the reactants into the radical cation[20] and that the addition of electron-rich substrates to ionized carbon−carbon double bonds in the gas phase occurs with great ease.[21] It appears that the size of the carbon ring in $C_n^{\bullet+}$ is of importance for the number of pyridine molecules that can be incorporated. By the reaction of $C_{12}^{\bullet+}$ with pyridine, only one of the two pyridines eventually attached is merged into the carbon skeleton while the second one is lost again during CID. The addition of a third pyridine to $C_{12}^{\bullet+}$ is not observed even at prolonged reaction times and increased partial pressure of pyridine in the FT-ICR cell. $C_{13}^{\bullet+}$ and $C_{14}^{\bullet+}$ do add a third pyridine molecule, and the reactive isomer of $C_{24}^{\bullet+}$ add up to five pyridine molecules. In the latter case the product ion $C_{39}H_{15}N_3^{\bullet+}$ generated by addition of three pyridine molecules does not eliminate pyridine on CID so that at least three pyridines can be incorporated into the large ring of $C_{24}^{\bullet+}$.

It is suggested that the second isomer of $C_{24}^{\bullet+}$, which gives the unreactive adduct ion $C_{29}H_5N^{\bullet+}$ with pyridine, still has the graphitic carbon skeleton of coronene. It has been discussed[7c] that planar graphitic structures of $C_n^{\bullet+}$ compete with monocyclic rings for $n \geq 30$ and that some of the peaks observed in the ion chromatogram of $C_n^{\bullet+}$ of this size, which were originally attributed to polycyclic structures,[22] are in fact due to graphitic structures when the $C_n^{\bullet+}$ is created by laser evaporation from

SCHEME 4



graphite. Furthermore, ab initio calculations indicate that even for $C_{24}^{\bullet+}$ a graphitic structure and a monocyclic structure may be isoenergetic.[23] In this work the $C_{24}^{\bullet+}$ are prepared from an ionized coronene derivative by successive elimination of the substituents at the rim of the graphitic carbon skeleton by CID. It has been shown that the molecular ions of smaller polycyclic perchloroarenes retain the graphitic structure during quite a number of elimination steps before a rearrangement to monocyclic $C_n^{\bullet+}$ eventually takes place.[7b] The energy imparted into the molecular ions of $C_{24}Cl_{12}$ during the MECA procedure for the elimination of the Cl substituents is difficult to estimate and corresponds certainly to a broad range of energies because of the multiple collisions occurring during ion excitation. Highly excited $C_{24}Cl_{12}^{\bullet+}$, which quickly lose all Cl substituents, contain certainly enough energy for a rearrangement of the carbon skeleton to the most stable monocyclic structure. However, there are certainly also $C_{24}Cl_{12}^{\bullet+}$ present that lose their substituents in a more gentle way by multiple excitation/de-excitation during the MECA procedure. In this case the original graphitic structure will be retained if it is quite stable and, more important, if a rearrangement to another even more stable structure from the intermediate ions $C_{24}Cl_x^+$ requires substantial activation energies exceeding that of further loss of Cl. Thus, graphitic $C_{24}^{\bullet+}$ should be present among the carbon cluster ions generated from $C_{24}Cl_{12}^{\bullet+}$ by MECA even if this structure is less stable than the monocyclic ring.

For further information the heats of formation $\Delta H_f(C_{24}^{\bullet+})$ for the monocyclic structure, the graphitic structure, and some intermediate structures have been calculated using PM3 (Scheme 4). One important mechanism of the isomerization of graphitic polycyclic structures of $C_nCl_x^+$ ions and $C_n^{\bullet+}$ into a monocyclic ring is ring opening by a retro-Bergman cyclization.[4,5,7] By use of this mechanism as a guide, the polycyclic structures of $C_{24}^{\bullet+}$ shown in Scheme 4 have been chosen as likely intermediates between graphitic $C_{24}^{\bullet+}$ and monocyclic $C_{24}^{\bullet+}$. The PM3 calculations result in large values of ΔH_f of these intermediate $C_{24}^{\bullet+}$ structures. Thus, graphitic $C_{24}^{\bullet+}$ and monocyclic $C_{24}^{\bullet+}$ are separated certainly by large barriers, and interconversion of these two isomers of $C_{24}^{\bullet+}$ is not an easy process.

At the first moment, it appears to be inconsistent that monocyclic $C_{24}^{\bullet+}$ reacts by addition of multiple pyridine molecules while graphitic $C_{24}^{\bullet+}$ with its many "dangling bonds"[7b,7c] at the edges adds only a single pyridine molecule. However, the picture of "dangling bonds" for graphitic C_n is not quite correct. In fact, 1,2-didehydrobenzene with an "aryne" triple bond is stabilized by more than 130 kJ/mol compared with the corresponding 1,2-diradical with its dangling bonds.[24] A similar stabilization per aryne bond is expected for dodecadehydrocoronene with its six aryne bonds. Hence, graphitic $C_{24}^{\bullet+}$ is better described by a structure with triple C−C bonds that are strained by bending, similar to the C−C bonds in monocyclic $C_{24}^{\bullet+}$. This may be one reason that both structures exhibit similar values of ΔH_f. However, both structures differ strongly in their electronic configuration. As mentioned before, monocyclic $C_{24}^{\bullet+}$ has two delocalized π-electron systems around the ring that are orthogonal to each other. As a consequence, the positive charge and the spin density due to the unpaired electron are delocalized in this radical cation. In contrast, the graphitic $C_{24}^{\bullet+}$ contains only the "normal" delocalized π-electron system of coronene from overlap of the 2p C orbitals perpendicular to the ring. The in-plane π electrons do not form a cyclic array of overlapping 2p C orbitals but form localized aryne bonds, and in the radical cation one of these localized bonds is ionized. Hence, the radical cation of graphitic C_{24} should exhibit a "vinyl cation" reactivity, explaining the attachment of only one pyridine molecule by its nucleophilic electron lone pair at the nitrogen atom to the carbenium center as observed. This attachment corresponds to the combination of an electrophile, the carbenium center, and a nucleophile, the pyridine lone pair, which is not expected to exhibit an activation energy along the reaction path. This Lewis acid/Lewis base combination explains the extraordinary, high reactivity of this $C_{24}^{\bullet+}$ isomer toward pyridine and the rate constant measured close to or at the collision-controlled rate limit.

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