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Reactivity of Carbon Cluster Ions with Benzene: 4-Fold Periodicity and Possible Aromaticity Effects

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Systematic studies of gas-phase carbon cluster molecules and ions have shown apparent aromaticity effects in several instances, manifested through 4-fold periodicities. The reaction rate constants of benzene with positively charged cluster ions from C_7^+ to C_{24}^+ provide a new illustration of such effects. These rate constants are substantial, but generally slower than the collision limit, and can be interpreted as a sensitive indicator of the relative reactivities of the cluster ions. A prominent 4-fold periodicity in reactivity is observed, with the formally antiaromatic C_{4k+1}^+ cluster ions showing enhanced reactivity. A general decline in reactivity with increasing cluster size is apparent. Second-clustering reactions with benzene are common, but slower, and show no systematic relation to the bare C_n^+ reactivities.

Carbon cluster molecules provide an interesting arena for studying aromaticity effects, since the carbon orbital overlaps, phases, and symmetries can play their roles without complicating effects from hydrogen or other substituents. A prominent illustration of an apparent aromaticity effect is seen in the ionization energies (IE) of the C_n neutrals.[1] The trend in IEs is smooth for C_7–C_{24}, except for the C_{4k+3} molecules, whose IEs are almost 1 eV below the trend line (Figure 4 of ref 1). This must be due to the favorable removal of the extra π electron to give the C_{4k+3}^+ cation family with a $4k + 2$ electron count in the π system corresponding to the HOMO.[3] The extra stability of the C_{4k+3}^+ ions is also reflected in the peaking at these masses in laser desorption/ionization (refs 1 and 2, and present results).

Similar 4-fold-periodic behavior is seen for the anions: Mass spectra for C_n^- production by laser desorption/ionization show peaking for the $4k + 1$ series over about the C_{10}^-–C_{30}^- range.[4,5] The ionization energies of the anions also show peaks for the $4k + 1$ series (superimposed on the more pronounced odd–even alternation).[6]

Just as aromatic molecules have characteristic exceptional stability and low reactivity, antiaromatic systems may display their unfavorable electronic character through exceptionally high reactivity. In the case of the medium-sized carbon cluster cations, we have found that the benzene reagent molecule gives a delicate discrimination of reactivities of the different clusters. A notable reactivity enhancement is clear for the formally antiaromatic C_{4k+1}^+ family, while the aromatic C_{4k+3}^+ family shows low reactivity. A number of other studies of C_n^+ reactions with organic neutrals have been reported.[7-19] The only previous indication of 4-fold-periodic reactivity is the enhanced C_{13}^+ and C_{17}^+ reactivity with acrylonitrile.[19]

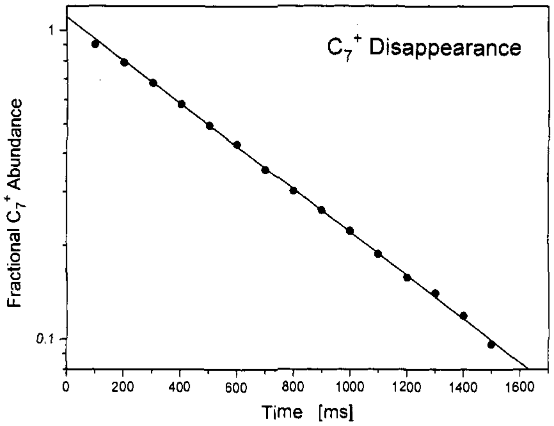

Figure 1. Logarithmic plot of disappearance of parent ion C_7^+. Benzene pressure was 2.5×10^{-8} Torr; N_2 pressure was 5×10^{-7} Torr.

The C_n^+ reactivities were observed by kinetic measurements of the ions contained in the ion cyclotron resonance (ICR) ion trap.[5] Following ion production by laser desorption/ionization of graphite (Nd:YAG laser at 532 nm), the ion of interest was isolated by ejection of all other C_n^+ species using a series of ICR ejection pulses. The kinetics of reaction of this chosen ion with benzene neutral were observed by standard ICR methods.

Figure 1 displays an illustrative kinetic plot, showing C_7^+ parent ion disappearance versus time. Because C_n^+ ions were usually produced with excess translational and internal energy, curvature of the kinetic plots at early times was common (as seen in Figure 1). To relax this energy, a bath gas was always used (N_2 at 5×10^{-7} Torr), and excellent straight-line logarithmic plots, extending to about 99% or more parent ion disappearance, were always observed for times longer than 100–200 ms. All reactions were measured at several benzene pressures over the range (3–40) $\times 10^{-8}$ Torr, and bimolecular rate constants were calculated. As an internal standard, the rate of C_9^+ was measured concurrently with each other cluster ion, and through this internal standardization the relative rate constants are quite reliable (typically ±15%). The absolute rate constant of C_9^+ disappearance was measured as $(23 \pm 7) \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, through which absolute rate constants may be assigned to all the reactions (uncertainties estimated).

Figure 2 shows the total disappearance rate constants for C_n^+. Immediately obvious is the 4-fold periodicity, with enhanced reactivity at C_{4k+1}^+. The reactivity falls off with increasing cluster size. In Figure 3 the same rate constants are displayed by families, showing the monotonic trend of rate constants within each family.

Table 1 shows the reaction rate constants and branching ratios for all the cluster ions. For the larger clusters ($n \geq 14$) the

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(3) The $4k + 2$ electron count rules are made complicated for cyclic C_n by the existence of two "π" electron systems derived from carbon 2p orbitals perpendicular to the chain, the ordinary out-of-plane π system, and the in-plane, or pseudo, π system. Corresponding orbitals made from these lie close in energy. These two π systems cannot both have $4k + 2$ electrons in a monocation or a monoanion. The "aromaticity" properties surveyed here correlate with the electron count in the π system which serves to construct the HOMO.

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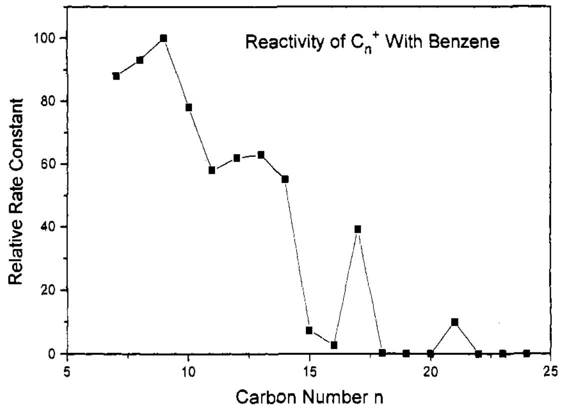

Figure 2. Total disappearance rate constants for C_n^+ reacting with benzene (relative to $C_9^+ = 100$).

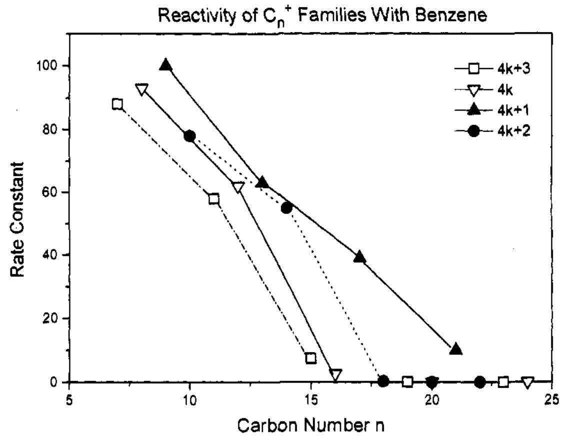

Figure 3. Rate constants as in Figure 2, displayed as family groups with 4-fold periodicity.

reactivity is simple, yielding only the simple adduct product $C_n(C_6H_6)^+$. For the smaller clusters a varying fraction of the products are the H-atom loss species $C_n(C_6H_5)^+$, along with a few additional reaction channels as noted in Table 1.

The formation of simple adduct at these pressures is presumably radiative association, as was also postulated by Zimmerman and Creasy[8] for naphthalene addition to several medium-sized C_n^+ clusters. Observation of radiative association for the smaller clusters implies a high binding energy. Applying the empirical estimation approach from ref 20 , the data suggest a decline in binding energy from 2 eV or more for the small cluster ions to about 1 eV or less for the large ones. This could reflect the decreasing electrostatic attraction between the benzene molecule and the delocalized charge of the larger clusters.

It is interesting that, although the overall reactivity (Figure 2) shows no sign of odd–even alternation, the H-atom loss reaction (Table 1) shows a striking alternation. We can speculate that the initial formation and stabilization of an ion–neutral complex is affected by aromaticity considerations and a $4k + 2$ rule, while the choice among subsequent reaction pathways in the complex is controlled by other (perhaps thermochemical) factors subject to odd–even propensity rules.

Table 1. Relative Reaction Rate Constants with Benzene[a]

carbon no.	total[b]	addn[c]	H loss[d]	second cluster[e]
5	66	0.0	66	23
6[f,g]	114	0.0	7.3	
7	88	0.0	88	3.2
8[g]	93	14.7	19.5	
9	100	0.0	100	2.4
10	78	78	0.0	0.4
11	58	50	8.0	0.4
12	62	62	0.0	0.5
13	63	26	37	0.5
14	55	55	0.0	6.1
15	7.4	7.4	0.0	2.9
16	2.6	2.6	0.0	0.03
17	39	39	0.0	2.5
18	0.3	0.3	0.0	0.23
19	0.1	0.1	0.0	nr[h]
20	nr			
21	10	10	0.0	nr
22	nr			
23	nr			
24	nr			

[a] Rate constants are scaled to C_9^+ assigned as 100. [b] Sum of rate constants for all reaction channels of C_n^+. [c] Simple association reaction. [d] Benzene addition with loss of H from the product. [e] Reaction of $C_n(C_6H_6)^+$ or $C_n(C_6H_5)^+$ to give $C_n(C_{12}H_{11})^+$. [f] Charge transfer was not significant except for C_6^+, for which it was the dominant channel. Rate constants for this ion are quite uncertain. [g] Ions C_6^+ and C_8^+ reacted with benzene through no less than 10 different channels. [h] The "nr" entry means that the relative rate constant is smaller than 0.01.

Monocyclic C_n^+ structures are stable over the C_7^+– C_{24}^+ series plotted here.[21] Linear structures are also stable[21] for the clusters C_7^+–C_{10}^+, and our suggested attribution of high C_9^+ reactivity to a cyclic antiaromaticity effect is clouded by the possibility of mixed isomer populations in this region. There are some indications that any linear components of these populations disappeared by charge transfer to benzene in the initial ion preparation period:[22] No sign of biexponential kinetic plots was found, as would have been seen if linear and cyclic ion reaction rates differed by more than a factor of 2. Such biexponential behavior is typical although not mandatory for mixed populations.[2,11-14,17] Moreover, the C_7^+–C_{10}^+ linear isomers would be expected to show significant charge-transfer reactions with benzene, whereas no charge transfer was observed after the initial ion preparation period. The basis of our suggestion of aromaticity effects is primarily the C_{11}^+–C_{24}^+ behavior, bolstered by the less clear-cut observation that the pattern also seems to hold true for C_7^+–C_{10}^+.

Second-clustering rate constants are smaller than for parent C_n^+ ions,

$$C_n(C_6H_m)^+ + C_6H_6 \rightarrow C_n(C_{12}H_{11})^+ \qquad [+H] \qquad (1)$$

With increasing C_n^+ size, the second-clustering rate constants show an irregular pattern. No correspondence with the corresponding C_n^+ rate constants is evident, and there is no sign of 4-fold periodicity. For aromatics larger than benzene, Zimmerman and Creasy[7] observed sequential attachments leading to large clusters, but we saw no tendency to attach more than two benzene molecules.

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