Reactivity Patterns of Carbon Cluster Cations with Nitrogen-Containing Molecules

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Abstract: Reaction kinetics of cyclic carbon cluster ions C_{10}^+ to C_{24}^+ with acrylonitrile, four isomeric C_4 nitriles, and pyrrole and pyridine are reported at 300 K. A prominent 4-fold periodicity was observed in reactivity with the five nitriles, with the highest reactivity being observed for the $n = 4k + 1$ series of C_n^+ cluster ions. This is interpreted as reflecting enhanced reactivity for the C_n^+ cluster ions which have an antiaromatic $4k$ electron count in the HOMO. The reactivity dropped off markedly with increasing cluster size, which is considered to indicate sharply decreasing cluster-ion/nitrile binding energy with increasing cluster size. By contrast, nearly all the cluster ions reacted rapidly with pyridine and pyrrole. A two-step mechanistic picture is discussed in which the overall reaction rate is controlled by the initial electronic interaction between the cluster ion and the neutral reactant, while subsequent bond-making/bond-breaking reactions are governed by the potential surface of the complex and are strongly affected by the available energy. Judging by reaction rates with acrylonitrile and crotononitrile, most of the carbon cluster ions generated by graphite ablation in the present work were identical with the corresponding ions previously generated by Sun *et al.* by ionization of perchlorohydrocarbons, although some differences in reactivity were found for ions of low reactivity.

Introduction

Much attention has been given to the larger (fullerene) carbon clusters, but the smaller clusters are also emerging as molecules with a rich, interesting, and distinctive chemistry. The series of carbon ions C_n^+ provides a complete sequential set of readily available clusters ranging in size from single-atom up into the fullerene range, which gives an exceptional field for exploring systematic physical and chemical variations with cluster size. Particularly intriguing to us are the 4-fold repeat patterns in the reactivity of the cluster ions, suggesting the manifestation of aromaticity and antiaromaticity effects which are not yet fully understood.

The small carbon cluster ions from about C_{10}^+ to C_{25}^+ are confidently believed to form a homologous series having the single-ring cyclic structure as the most favored structure.[1−4] Accordingly trends in stability and reactivity along this series can be characterized without the extensive isomeric mixing that clouds systematic comparative studies of smaller C_n^+ ions (linear structures) and larger ones (polycyclic and fullerenic structures). It was recognized early[5−10] that there are magic numbers at C_{4k+3}^+ which are particularly favorable for formation of carbon

cluster ions, and these were naturally ascribed to electronic orbital-occupation effects, for instance *via* extended Hückel theory.[11] The point of significance is that these favored (aromatic) cluster sizes correspond to $4k + 2$ electron counts in the π HOMO system. Another manifestation of such effects was noted by Lifshitz *et al.* in discussing binding and dissociation energies in carbon cluster cations, where they introduced the suggestive "aromatic/antiaromatic" terminology.[12] In early observations of selective reactivity effects, McElvany *et al.* found enhanced reactivity of C_{13}^+ with several small molecules (acetylene, ethylene, HCN).[13,14] The role of 4-fold periodic effects in cluster reactivities became clearer, and in particular the enhanced reactivity of the "antiaromatic" series of monocyclic clusters C_{13}^+, C_{17}^+, and C_{21}^+, as a result of parallel studies in our laboratory[15] and in the laboratory in Bielefeld.[16−18] An indication of 4-fold-periodic reactivity was found in the observation by Sun *et al.*[16] of reactivity peaks for C_{13}^+ and C_{17}^+ with acrylonitrile. These authors have more recently reported similar results with crotononitrile[17] (where they discussed the importance of aromaticity and antiaromaticity), and with chloropropenes.[18] Our group[15] reported the reactivity pattern of the complete series of C_n^+ for $n = 10$ to 24 with benzene, showing strong peaks for C_{13}^+, C_{17}^+, and C_{21}^+, as well as reactivity minima for C_{11}^+, C_{15}^+, and C_{19}^+. This study of the complete series gave a particularly dramatic view of the 4-fold-periodic reactivity pattern for the monocyclic cation clusters, and our interpretation emphasized the connection between the reactivity peaking and a postulated antiaromatic character for the $n = 4k$

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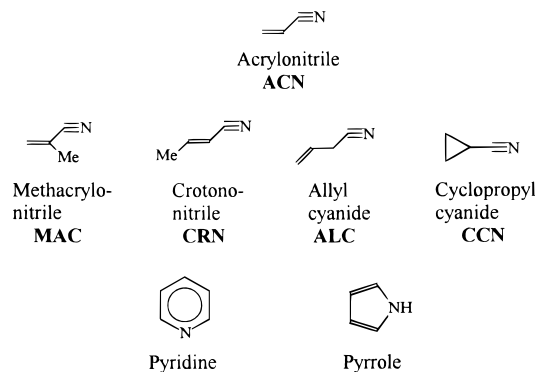
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Chart 1

Acrylonitrile
ACN

Methacrylo-
nitrile
MAC

Crotono-
nitrile
CRN

Allyl
cyanide
ALC

Cyclopropyl
cyanide
CCN

Pyridine   Pyrrole

Table 1. Heats of Formation and Ionization Energies for the Neutral Reactants Used in this Study[a]

molecule	$\Delta H_{f,298}°$ (kcal mol^{-1})	IE (eV)
	C$_3$ Nitrile	
ACN	184	10.9
	C$_4$ Nitriles	
MAC	130	10.34
CRN	151	10.23
ALC	155	10.2
CCN	184	10.25
	Nitrogen Heterocycles	
pyrrole	108	8.2
pyridine	138	9.25

[a] Reference 19.

+ 1 series of ions. We report here an extensive reactivity study for a set of nitrogen-containing compounds that extends and clarifies the importance of antiaromatic character in C$_n^+$ reactivity.

The C$_n^+$ ions used by Sun *et al.*[16-18] were generated by dissociative ionization of perchlorohydrocarbons, while those used by our group come from graphite ablation, so an important further feature of the present study is a detailed comparison of the reactivity of the cluster ions from these different sources.

Seven nitrogen bases were used as neutral reactants in this study, as shown in Chart 1 with the abbreviations used to represent them here. The four isomeric C$_4$H$_5$N nitriles, referred to below as the "C$_4$ nitriles," are of particular value for probing the reaction mechanisms, since they have the same mass, and similar polarizabilities and ionization energies and share the nitrile functionality. The heats of formation and ionization energies of these compounds will be of interest in the discussion below, and are given in Table 1.

Experimental Section

All experiments were done on a home-built FT-ICR instrument with a 1.4 T electromagnet employing an IonSpec data system. Pressures varied from 1×10^{-8} to 100×10^{-8} Torr in order to bring the particular reactions under study into a convenient rate regime. Pressures were read from an ionization pump for which the pump current is known by experience to give reasonably accurate pressures for organic molecules.

Carbon clusters were produced by a direct laser vaporization of a piece of graphite mounted on one of the trapping plates of the ICR cell. The laser beam from a Nd:YAG laser (∼1 mJ at 532 nm) was focused on the graphite surface. This efficiently produced clusters from C$_3^+$ to C$_{24}^+$. A cluster of interest was selected by a series of cyclotron ejection pulses. Reactant neutral was constantly fed into the vacuum chamber through a leak valve. Twenty to 200 transients were averaged depending on the intensity of the signal.

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In a series of experiments with a given neutral reactant, the chemistry of each cluster was first determined separately, following which the reaction rates for the different C$_n^+$ species were measured simultaneously (except for cases of coincident product-ion masses). This assured that the relative rate constants were accurate for reaction with any given neutral. One or two clusters (usually C$_{11}^+$ and/or C$_{15}^+$) were chosen as reference clusters for determination of the bimolecular rate constant. For these reference cases, reaction rates were measured at a number of different pressures, and a bimolecular rate constant was determined from a plot of rate vs pressure. The rate constants for the other clusters were then determined relative to these by peak height comparisons. Repeatability of rate constants in consecutive experiments was better than 30%, which is a reasonable estimate of the precision of relative rate constants for a given neutral.

Pressure comparisons (and corresponding rate constant comparisons) between different neutrals are not assured to better than a factor of 2, although this series of similar reactants may be expected to be more accurately comparable than this, and might be considered relatively accurate within a factor of 1.5 across the series of nitriles. The absolute bimolecular rate constants could be in error by as much as a factor of 2 due to pressure uncertainties. As the instrument was configured for exclusive laser desorption/ionization of the graphite sample, no convenient way was available for anchoring the pressure calibration to known reaction rates of more conventional ions. A good indication that the absolute rate constants were in fact more accurate than these conservative uncertainties is provided by the excellent absolute agreement of the results for acrylonitrile and crotononitrile with the measurements of Sun et al.,[16,17] which they considered to have an absolute accuracy of 20%. Given the assumption (see below) that the same reactant ion structures are involved in these different studies, the agreement of rate constants helps to validate the pressure assignments and absolute rate constant calibrations of the present work.

Carbon cluster ions produced by direct laser vaporization are internally and kinetically excited. Additional, unknown kinetic energy is added by off-resonance cyclotron excitation during the sequence of radio frequency ejection pulses used to isolate the ion species of interest. Thus at the beginning of the reaction period the ions have poorly characterized, and perhaps substantial, excess velocity and internal energy. The effect of this excitation was routinely evident in that the bimolecular association rate constants were initially lower than their long-time asymptotic values, and branching to high-energy product channels was seen at short times. As time passed and the ions relaxed via collisional and radiative cooling, the reaction rates leveled off to steady values, and branching to high-energy channels decreased, with all product channels other than simple association disappearing in most cases when the ions had had time to thermalize to 300 K.

To obtain thermal-ion rate constants and branching ratios some laboratories introduce a pulse of inert gas at the beginning, and observe the chemistry of the thermalized ions after the collision gas has pumped away. An effective alternative is the software approach used in the present work, in which the reactions are monitored from the very beginning and the long-time asymptotic values of rate constants and branching ratios are taken to correspond to thoroughly thermalized reactant ions. To carry this procedure out in practice, the instantaneous rate constants and branching ratios were calculated by numerical differentiation of the ion abundance-versus-time curves. Illustrative plots of rate constants and branching ratios versus reaction time are shown in Figure 1. In the usual case where these curves leveled off convincingly to steady values at long reaction times, the long-time values were assigned with confidence as corresponding to reactants thoroughly thermalized at 300 K.

Most of the reactions are observed to be inefficient, so that many unsuccessful collisions of the ion with neutral reactant molecules occur before a fruitful collision, allowing ample opportunity for the ions to equilibrate their internal, rotational, and translational temperatures with the bath of 300 K neutrals. However, a problem encountered with this approach in some cases, as for instance C$_{10}^+$ reacting with the C$_4$ nitriles, was that the reaction efficiency was so high that the reactant ions reacted away before they could thermalize. This was countered by running at very low reagent gas pressure to allow more extensive radiative cooling of the internal degrees of freedom of the ions before their first collision, and also by diluting the reagent gas with inert bath
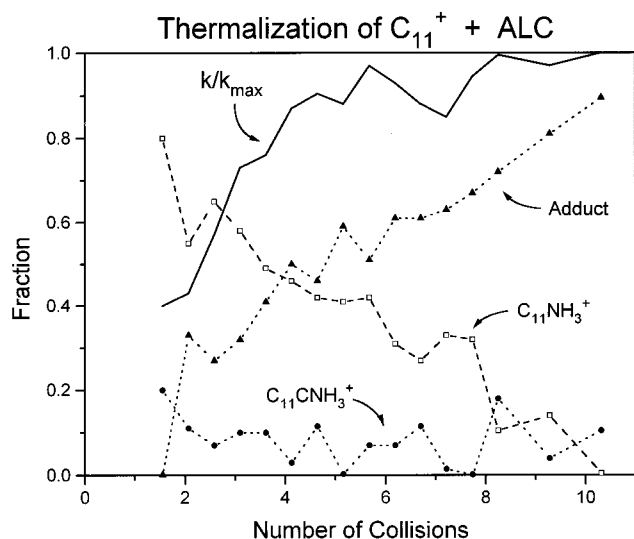
Figure 1. Plots showing the evolution of the kinetics of the ALC/C_{11}^+ system with time following the laser pulse. The horizontal axis (which is essentially the time after the ion formation laser pulse) is expressed as the calculated number of orbiting collisions of the C_{11}^+ reactant ions with neutral molecules since ion formation. (The collision rate was of the order of 0.3 s^{-1}.) The solid line shows the total reaction rate (disappearance rate) of C_{11}^+, expressed as a fraction of the asymptotic final rate constant k_{max}. The lines with symbols show the instantaneous branching ratios to the three main products, namely the full adduct $C_{15}H_5N^+$ and the two indicated elimination products. These are expressed as the fraction of the total instantaneous product formation belonging to each of the three product ions at the indicated time.

gas (nitrogen), typically at a 10:1 ratio, to allow collisional relaxation of both internal and translational ion excitation before the reactive collision.

If the reactant ion population consists of a mixture of isomers with different reaction rates, this approach will mask the true situation, since the faster-reacting isomer will appear just as if it were a fraction of hot ions, reacting fast and disappearing at long times. (However, note that this hypothetical situation would be atypical, since hot ions normally react slower, not faster, than thermalized ions.) This confusion between isomer mixtures and non-thermalized ion populations is readily sorted out by dilution with inert bath gas, since hot-ion relaxation will be accelerated by bath-gas collisions, while differential isomer reactivity will be insensitive to added bath gas collisions.

The rate constants reported below come from satisfactory single-exponential fits to the long-time portion of the parent-ion decay curve, and thus represent the sum of all reaction channels in cases where there is branching to more than one product. For a given neutral reactant, the rate constants for different cluster ions were compared directly by simultaneous observation, so these numbers are accurately comparable. Thus, for example, the reactivity of C_{22}^+ with ALC can be reliably taken as 3 times that of C_{18}^+ (within the quoted 30% uncertainty). Comparison of values for different neutral reactants is less accurate because of the uncertainty in relative pressure calibrations noted above. Thus among the four C_4 nitriles it might be tempting to say, for instance, that CCN is on the whole somewhat more reactive than the others, but we would not consider such differences to be reliable within the pressure uncertainties. On the other hand, the factor of 10 lower reactivity of ACN compared with the C_4 nitriles is definitely much greater than the pressure uncertainties, and is certainly significant.

Samples of compounds were obtained commercially from Aldrich Chemical (crotononitrile, acrylonitrile, cyclopropyl cyanide), Fluka (allyl cyanide), Fisher (pyridine), and Eastman (methacrylonitrile, pyrrole), and were used without further purification except for 3 freeze/pump/thaw cycles.

Results and Discussion

Reaction Patterns and Kinetics. The reaction rate constants for thermalized ions are listed in Table 2. The reactivity patterns

Table 2. Bimolecular Reaction Rate Constants (Parent Ion Disappearance Rate Constants) for Reactions of Carbon Cluster Ions with Nitrogen-Containing Neutrals[a,b]

	ACN	MAC	CRN	ALC	CCN	pyrrole	pyridine
LCR[c]	29.1	26.4	30.9	28.0	27.9	16.0	17.5
C_{10}^+	2.7	39	24	46	32	d	6
C_{11}^+	0.42	6.1	5.1	5.7	9.2	25	74
C_{12}^+	0.7	8.2	11	36	13	31[e]	74
C_{13}^+	4.0	20	19	35	38	27[e]	56
C_{14}^+	0.5	2.3	2.2	2.8	4.6	25	69
C_{15}^+	0.07	1.1	1.1	1.0	2.7	22	65
C_{16}^+	<	0.18	0.17	0.05	0.5	28	61
C_{17}^+	1.4	8.5	8.2	7.6	25	21	74
C_{18}^+	<	0.06	0.06	0.03	0.2	32	67
C_{19}^+	<	0.05	0.08	0.05	0.3	18	48
C_{20}^+	<	<	0.05	0.08	<	22	39
C_{21}^+	0.1	2.2	2.9	5.3	6.7	37	46
C_{22}^+	<	<	<	0.09	<	23	46
C_{23}^+	<	<	<	<	<	12	30
C_{24}^+	<	<	<	<	<	9	22

[a] Rate constants in units of 10^{-10} cm^3 molecules^{-1} s^{-1} at 300 K. [b] Relative rate constant ratios down the column for one reactant neutral are given a relative uncertainty of 30%. Rate constant comparisons between different nitriles are considered accurate within a factor of 1.5, while comparisons of pyridine or pyrrole with other neutrals are probably unreliable. The uncertainty in the absolute rate constant values is discussed in the text. The "<" symbol indicates a rate constant below the limit of measurability, which was somewhat variable, but typically about 0.01. [c] Predicted Langevin orbiting rate constants, calculated including dipole moment effects according to ref 20. Since these are not a strong function of cluster mass, they are given here for an average cluster in the middle of the range. A number of observed rates are larger than the calculated orbiting rates. This may reflect large hard-sphere collision cross sections, or errors in pressure calibration. For pyridine, in particular, the very high calculated rate values relative to the Langevin value clearly suggest a pressure calibration error, and the absolute calibration of these pyridine rate constants should be considered as fixed only to the extent that these reactions are certainly highly efficient. [d] Only charge transfer was observed. [e] These two cases, unique among the thermal-ion reactions described here, exhibited rapid charge transfer in addition to association reactions. The rate constants given are estimates of the association reaction component, excluding charge transfer, but are very uncertain due to uncertainties in the data analysis.
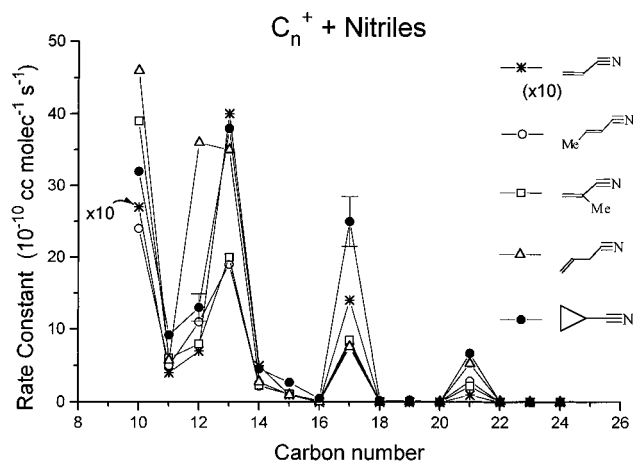
Figure 2. Rate constants for reactions of carbon cluster ions C_{10}^+ to C_{24}^+ with five nitriles. The quantity plotted is the reactant ion disappearance rate constant, equal to the sum of all product channels. (The example error bars correspond to the relative uncertainties between different cluster ions. The absolute uncertainties are larger, as discussed in the text.)

are displayed in Figure 2 for the five nitriles and in Figure 3 for the cyclic neutrals. The reactivity pattern for the nitriles is strikingly similar, showing prominent peaks for the antiaromatic clusters C_{13}^+, C_{17}^+, and C_{21}^+. This set of nitriles gives the
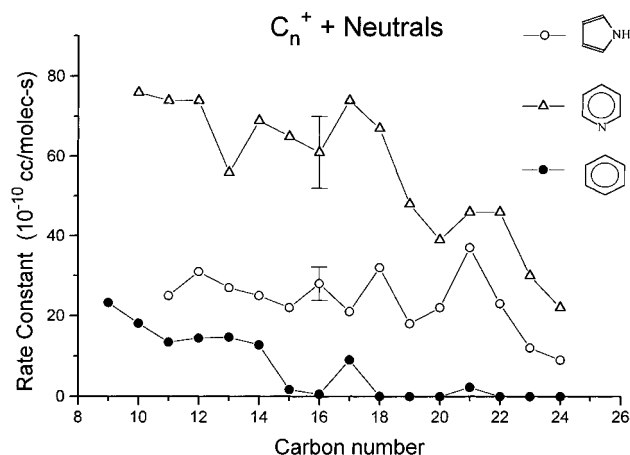
Figure 3. Reactivity patterns for the two nitrogen heterocycles, as well as for benzene (ref 15).

Table 3. Reaction Channels (Other Than Simple Association) for Thermalized Ions[a]

neutral fragment lost	neutral reactant	
	CRN	ALC
H	C_{10}^+ (50%), C_{12}^+ (40%)	C_{10}^+ (30%), C_{12}^+ (55%)
HCN	C_{10}^+ (30%)	C_{10}^+ (40%)
C_3H		C_{14}^+ (35%)

[a] Each entry indicates that cluster C_n^+ undergoes the indicated elimination reaction, and the percent figure in parentheses indicates the fraction of product ions in this channel. The balance of the products in each case follow the simple association channel to total 100% for each pair of reactants. The percent branching values can be considered uncertain to ±10%.

strongest display of enhanced antiaromatic reactivity thus far seen. The pattern is considerably more prominent than that for benzene.[15]

Pyrrole and pyridine are clearly more reactive than the nitriles, reacting rapidly with nearly all clusters. This high reactivity apparently washes out any possible aromaticity effects in the reactions with these two neutrals. These results also indicate that the higher cluster reactivity with the nitrogen heterocycles is not necessarily related to the presence of a negatively charged nitrogen, since the dipole moment in pyrrole actually has its positive pole at the nitrogen end, yet this compound is among the most reactive with these ions.

For the most part the reactions of thoroughly thermalized cluster ions yielded the simple association ion as the only significant product. The exceptional cases for which significant neutral-elimination channels were observed are listed in Table 3.

In contrast to the thermalized ions, cluster ions which did not have their internal and translational energies thermalized showed a wide variety of dissociative products, as well as depressed overall rate constants, which are listed in Table 4. It seems probable that these hot-ion reactions were driven by

translational energy, since they were suppressed by a few thermalizing collisions but were not suppressed by low-pressure radiative ion cooling. Figure 1 shows typical thermalizing behavior, in this case for C_{11}^+ reacting with ALC. At the shortest times following ion production, the total reaction rate constant is low, and the product distribution is dominated by the elimination products. As the reactant is thermalized by successive collisions the total reaction rate rises to its final value, and the fraction of association product ions $C_{15}H_5N^+$ rises to unity.

Tables 3 and 4 appear to tell a similar story in the sense that certain combinations of cluster ions with neutrals can undergo rearrangement chemistry with sufficient energy release to give expulsion of a neutral fragment. The elimination reactions reported for thermal ions in Table 3 are also prominent for hot ions in Table 4. The difference is that with the hot ions a wider range of cluster ions show such reactions, and many additional reaction channels become available.

There is an obvious overall fall-off in reactivity for the nitriles as cluster ion size increases. The two factors mainly affecting association efficiency are the number of degrees of freedom of the metastable collision complex and the depth of the complex binding well. Since the increasing number of degrees of freedom of the complex is expected to give quite a strong increase in the efficiency of radiative association with increasing size, these results indicate that the binding well becomes much shallower as the cluster ion size increases, perhaps reflecting an increasingly delocalized charge distribution in the larger cluster ions.

In these results shown in Table 2 and Figure 2, there is no indication of an even−odd alternation pattern in the total reactivity. The 4-fold periodicity of reactivity is the dominant pattern. This leads us to the interpretation outlined below that the initial cluster-ion/neutral interaction is dominated by electronic effects, reflected in the 4-fold repeat pattern characteristic of aromatic/antiaromatic character. On the other hand, the patterns of products reported for the elimination reactions in Table 4 are clearly different for even and for odd clusters. The most characteristic reactions for even cluster ions are seen to be H• loss and HCN loss, whereas C_4H_2 loss is the usual reaction observed for odd cluster ions. The striking even−odd differences in reaction types observed here are analogous to those seen by Sun *et al.*[17,18] in their CID reaction chemistry, although a greater variety of reactions was observed in the present hot-ion reactions. A speculative rationalization of these even−odd reaction patterns has been proposed and discussed at length by Sun *et al.*,[17,18] based on the distinction between acetylenic and cumulenic bonding in the even and odd clusters. It seems likely that similar ideas can account for the present observations, although we are not prepared to propose detailed mechanisms here.

Comparison with Results using C_n^+ from Perchlorohydrocarbon Sources. The present results give important so-

Table 4. Reaction Channels (Other Than Charge Transfer and Simple Association) for Hot Ions[a]

neutral fragment lost	neutral reactant						
	ACN	MAC[b]	CRN	ALC[c]	CCN	pyrrole[d]	pyridine
H		10	10, *12*	10, *12*, 14	10	11, *12*	11, 13
CN		10	10, 12	*10*, 12	10	12	
HCN	*10*	*10*	*10*, 12	*10*, 12	*10, 11*	*11*, 13, 15, 17, 19	10, *11*, 12, 14
C_3N				*14*			
C_4H_2[e]			11	*11, 13, 15, 17*			

[a] Channels in boldface/italics dominate the product distribution for their respective reactants. The numbers entered in the table are the carbon numbers n of C_n^+. [b] Minor loss of CH_3 and C_3H_4 with C_{10}^+. [c] Minor loss of C_3H_2 with C_{11}^+, loss of C_3H_4 with C_{10}^+. [d] Minor loss of C_4H_3 with C_{11}^+. [e] Note that this channel corresponds to NH_3 addition to the cluster ion.

Table 5. Comparison of the Present Kinetic Results with Results from Refs 16 and 17, Which Used Carbon Cluster Ions Generated from Perchlorinated Hydrocarbons (Rate constants in units of 10^{-10} cm^3 molecules^{-1} s^{-1})

	acrylonitrile		crotononitrile	
	present[a]	ref 16[b]	present[a]	ref 17[b]
C_{10}^+	2.7	2.8	24	11
C_{11}^+	0.42	0.56	5.1	3.3
C_{12}^+	0.7	0.70	11	12
C_{13}^+	4.0	7.1	19	12
C_{14}^+	0.5	0.25	2.2	<0.01
C_{15}^+	0.07	0.12[c]	1.1	<0.01
C_{16}^+	0	0.09	0.17	<0.01
C_{17}^+	1.4	2.0	8.2	8.6
C_{18}^+	0	0	0.06	<0.01
C_{19}^+	0		0.08	
C_{20}^+	0	0	0.05	<0.01

[a] Relative uncertainties 30%. The absolute uncertainties are larger, as discussed in the text. [b] Uncertainties reported to be 20%. [c] It was reported in ref 11 that only 44% of the C_{15}^+ ions were reactive, but in the present study the entire population was found to be equally reactive. This may reflect a residual population of ions formed in ref 11 that do not rearrange to the normal monocyclic C_{15}^+ structure.

lidification to the less complete results from Sun *et al.*[16,17] Looking at the cluster ions of reasonably high reaction efficiencies, the present rate constants for ACN and CRN are in satisfactory agreement with those of Sun *et al.* for the ions in common to the studies of the two laboratories, as shown in Table 5. This is a strong indication that these ions in their studies do indeed find their way to the stable monocyclic structures, as they postulated. The 4-fold periodic peaking suggested by their data for C_{13}^+ and C_{17}^+ is confirmed, and extended by the present clear peak at C_{21}^+. Furthermore, the observation of the same reactivity pattern with use of each of the series of nitriles studied here strengthens the conclusion that the 4-fold periodicity is not dependent on the nature of the particular neutral reaction partner, but is dependent on the carbon cluster ion properties.

On the other hand, the agreement is not good for ions of lower reactivity, and in particular several ions found to react with CRN at significant rates in the present study were reported to be unreactive in ref 17. These differences could be interpreted as suggesting structural differences for these low-reactivity carbon cluster ions depending on the method of production. However, because experimental conditions differ between these two quite different setups, and because the FT-ICR technique can have difficulty quantifying small peaks near the baseline noise, we would be reluctant to conclude that these observed differences actually reflect ion structure differences rather than artifactual experimental differences.

Association Rates and Binding Energies. Recent work has encouraged the idea that the magnitude of the radiative association rate constant gives a good quantitative idea of the binding energy of the association complex.[20,21] Simple modeling, based on the principle that hydrocarbon-based systems are generically similar to a useful first approximation, has been successful in making this relation in a number of diverse systems. This semiquantitative success in estimating bonding energies is attributable to the very sensitive dependence of the association rate on the binding energy, so that a single generic theory gives bonding energy estimates for a variety of complexes with a confidence of a few tenths of an electrovolt. The prescription for doing this was given in ref 21a, but a recent reevaluation with a more convincing canonical phase space
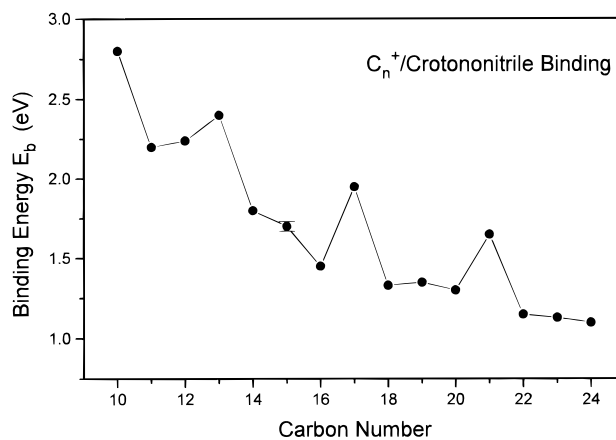
Figure 4. Binding energies for the C_n^+/CRN system, derived by kinetic analysis of the radiative association rate constants. (The example error bar is derived from the relative uncertainty of 30% for the rate constant ratios between different C_n^+ species. The absolute uncertainty of the binding energies is certainly much larger, perhaps ±20%.)

theory formulation has been described,[22] and is thought to be more reliable. (This new formulation gives binding energies about 20% higher for these systems than the formulation of ref 20.) The estimated binding energies for crotononitrile are displayed in Figure 4, and are typical of the C_4 nitriles. As expected, the exceptionally high C_{4k+1}^+ rates are reflected in corresponding peaks in estimated binding energy.

The rate constants for ACN are significantly slower than those for the C_4 nitriles. It is interesting to consider whether this difference reflects distinctive chemistry of ACN, or whether the difference can be ascribed to the smaller number of degrees of freedom of the complex along with a believable decrease in binding energy. By using the theoretical framework described above, it can be estimated that ACN should give lower association efficiencies by a factor of 2−3 due to the smaller number of degrees of freedom. From Table 2 it is seen that the ACN rates are actually slower than the C_4 nitriles by more like a factor of 10 on average, which suggests that ACN is more weakly bound to typical C_n^+ clusters than the C_4 nitriles by ∼0.15 eV. This modest difference is within the range that could be rationalized by differential electrostatic effects, and it seems unnecessary to postulate basically distinctive chemical effects for the ACN case.

Charge Transfer. Almost all of the hot ions gave at least some charge transfer to the neutral molecules, with this channel being more pronounced for the smaller cluster ions (C_{10}^+ to C_{13}^+). However, according to the results of Bach and Eyler,[23,24] all of the neutrals except pyrrole have higher ionization energies (Table 1) than the recombination energies of any of these cluster ions, and as expected no charge transfer was observed for thermalized reactant ions. In cases where charger transfer was observed for the hot ions, it disappeared rapidly with cooling of the ions and was negligible before any clustering reactions commenced.

The ionization energy of pyrrole (8.2 eV) is lower than or similar to the recombination energies of many of the nonaromatic cluster cations. The highest cluster ion recombination energies are reported as C_{10}^+ (9.08 eV), C_{12}^+ (8.50 eV), and C_{14}^+ (8.50 eV), and charge transfer to pyrrole for these ions would be likely. In fact, charge transfer was the only reaction

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for C_{10}^+, and was a significant competitor to association for C_{12}^+ and C_{13}^+, but was insignificant for C_{11}^+ (7.45 eV) and for all clusters larger than C_{13}^+. It has been observed in other radiative associations involving π complexation that the association channel can compete successfully with a slightly exothermic charge transfer channel,[24] so the observation of such a competition for C_{12}^+ is not surprising. However, the substantial charge transfer observed for C_{13}^+ (8.09 eV) and the absence of charge transfer for C_{14}^+ are both at variance with the expectations based on Bach and Eyler's best values,[23] and suggest that the ionization energies of these two ions might be reevaluated. Otherwise the charge transfer results for pyrrole are consistent with expectations.

Second Clustering. All of the product ions (both simple adducts and elimination products) underwent further reactions. These secondary reactions proceeded either by attachment of the full neutral molecule or often by attachment with elimination of a single H$^\bullet$ atom. Only acrylonitrile gave more extensive fragmentation of the second-clustering complex. A third neutral molecule was often attached to the second-clustered ion, but in no case (even the highly reactive heterocyclics) was a fourth neutral observed to cluster to the complex.

It is notable that these second-clustering processes showed none of the 4-fold periodicity in reactivity that is so prominent for the first-clustering processes. Neither was there any obvious odd−even alternation in reaction patterns. This disappearance of selectivity of the ion reactivities after addition of the first ligand might suggest that the more highly reactive C_n^+ ions (viz., the antiaromatic members of the series) may undergo rearrangement reactions with the first ligand, as suggested in the next section, leading to a lowering of their reactivity and loss of selectivity for a subsequent ligand.

Overall Mechanistic Picture. We can distinguish two different types of chemistry involved in these reactions: the association chemistry, which decreases with increasing kinetic energy; and the elimination chemistry, which is activated by excess kinetic (and perhaps internal) energy. While the association rates are strongly suppressed by excess kinetic and/or internal excitation energy of the reactants, they are apparently unaffected by the latent energy that can be released by disrupting the covalent structure of the nitrile. (The variation in latent energy is indicated by the differences in heat of formation values for the isomeric molecules, as shown in Table 1.) Thus there is not an experimentally significant systematic change in association efficiencies in going from MAC to CRN to ALC, although the available latent energy along this progression increases by 25 kcal (Table 1). In contrast, the elimination chemistry becomes more prominent, with more available channels and higher rates, as we vary the reactant along this same series (MAC to CRN to ALC). Thus it appears that once rearrangement processes begin, the latent energy of rearrangement of the nitrile becomes mobilized to assist expulsion of a neutral fragment.

On the other hand, CCN shows elimination chemistry quite similar to the low-energy MAC structure. Evidently the substantial latent strain energy of the cyclopropyl ring is not available to drive elimination reactions, suggesting that the cyclopropyl group retains its integrity.

The most straightforward picture to accommodate these contrasting types of behavior is a two-step reaction sequence. In the first step, a metastable noncovalently bound complex is formed in which the neutral reactant structure remains intact. This complex either redissociates to reactants or stabilizes (by photon emission or collision) to give a stable complex. As has been discussed often, the efficiency of formation of stabilized complex drops off sharply with increasing kinetic and internal energy of the reactants. In the second step, bond breaking chemistry occurs to yield rearranged structures and to mobilize the latent rearrangement energy of the neutral reactant. These rearrangements may often result in expulsion of a neutral fragment, but this need not necessarily be true. The evidence indicates, first, that the decision whether the metastable complex will stabilize or redissociate to reactants is made before the initiation of rearrangement processes and, second, that the initiation of rearrangement steps leading to neutral fragment expulsion is strongly promoted by excess kinetic (and perhaps internal) energy. Such a two-step mechanism is bolstered by observations in the chloropropene systems,[18] in which the elimination channel is apparently open to all the combinations of cluster ions and neutrals, yet reaction is much slower than the collision rate in most cases, and is strongly enhanced for the antiaromatic C_{13}^+ and C_{17}^+ cluster ions. This again may point to stabilization of an initial noncovalent complex as the overall rate-determining process.

Most of the thermal-ion reactions result in nondissociative adduct complexes. To obtain more insight into whether rearrangements occur within these complexes, some limited collision-induced dissociation (CID) experiments were done to try to probe the structures of the adducts. The adduct ions from C_{11}^+ and C_{15}^+ reacting with CRN were subjected to mild CID conditions with N_2 collision gas. The only CID product observed in each case was the regenerated parent ion, C_{11}^+ or C_{15}^+, respectively. In contrast, the elimination product ions C_{11}-NH_3^+ and $C_{11}CNH_3^+$, derived by hot-ion reactions from C_{11}^+, gave no fragmentation when subjected to the same CID conditions. This is an indication that the observed fragmentation of the two adduct ions reflects particularly weak binding in a noncovalent complex. At least for these two cases, these CID observations suggest that rearrangement processes do not occur in the nondissociative adduct complexes.

The sharp contrast between the 4-fold pattern of total reactivities and the odd−even pattern of the elimination reaction products gives support to the suggestion that two different mechanistic steps are involved in this chemistry. In the complex formation and stabilization step, binding of the nitrile to the intact cluster ion is influenced by the electronic properties of the cyclic C_n^+ ion in the pattern we ascribe to aromaticity effects. In the subsequent rearrangement chemistry, the nature of the products is affected by the differing carbon-chain properties for odd and even chains, perhaps in the manner described by Sun *et al.* in refs 17 and 18.

A further argument favoring noncovalent binding of the initially formed complex with nitriles is the sharp fall-off in rates and inferred binding energies for larger clusters. If the initial attachment of the nitrile to the carbon chain were controlled by chemical attack involving covalent bond breaking and formation, it would be reasonable to expect similar observed attachment efficiencies regardless of cluster size. The strong cluster size dependence argues instead for control by electrostatic interactions as expected for initial rate-determining formation of a noncovalent complex.

Conclusions

The most striking aspect of these results is the dominance of the 4-fold periodic variation in C_n^+ reactivity with the nitriles. The suggestion that the enhanced reactivity of the $4k + 1$ series of cluster ions reflects antiaromatic character in their electronic structure is a provocative hypothesis that should stimulate further theoretical analysis.

The reaction rate constants and branching ratios for acrylonitrile and crotononitrile are in good agreement with the more limited values previously reported for the cluster ions having reasonably high reactivities. This agreement confirms the lack of structural memory effects following production of the carbon cluster ions by the Sun/Grützmacher/Lifshitz method. For cluster ions of low reactivity there are substantial differences in rates, but whether this is due to structural differences or to experimental artifacts is uncertain.

A distinction is drawn between the characteristics of two steps in the reaction processes. It is postulated that an initial encounter to form a noncovalent complex occurs, with the overall reactivity being determined by the probability that this complex will be stabilized before reversion to reactants. Depending on the system and on the energy available, this complex may proceed further through rearrangement processes to covalently bound species, with the possibility of an accompanying expulsion of a neutral fragment.

Some questions about the aromaticity effects on reactivity have been sharpened rather than answered by the present results, and offer opportunities for further experiments and thinking. If the effects discussed are, as postulated, a reflection of the aromatic properties of $4k + 2$ electrons in the HOMO (or, conversely, the antiaromatic properties of $4k$ electrons in the HOMO), it may be surprising that they persist with such force up to at least C_{21}^{+}, since it seems unlikely that such large rings remain rigidly planar. So one question to address is whether the effects observed in these systems reflect the topological aromaticity properties of the closed carbon chain as opposed to the geometrical properties of planar cyclic π orbitals. Another area of uncertainty is the means by which the 4-fold periodic properties of the carbon rings operate to modulate the reactivity. The link might be the modulation of the thermodynamic stability along the series of clusters; or in a different spirit it might be the favorable or unfavorable interaction of electron clouds or frontier orbitals as the reacting partners interact to form the collision complex.

The existence and nature of potential barriers separating the initial association complexes from the subsequent rearrangement products is addressed in only the most cursory way by the probes described here. More incisive probing of these potential surfaces offers interesting future opportunities.

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