Novel Charge-Transfer Electron-Detachment Reaction for the Production of Naphthalene Dications at Thermal Energy

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The reactions of $He^{+\bullet}$, $Ne^{+\bullet}$, and $Ar^{+\bullet}$ with naphthalene have been studied with a selected-ion flow tube at 294 K and 0.35 Torr. The major product in the reaction of $He^{+\bullet}$ occurs at m/z 64, which is attributed to $C_{10}H_8^{2+}$. The occurrence of this reaction is in agreement with the appearance potential for formation of $C_{10}H_8^{2+}$ from naphthalene. The efficiency of this apparent "charge-tranfer electron-detachment" process for $He^{+\bullet} + C_{10}H_8$, and its recently reported occurrence for $He^{+\bullet} + C_{60}$ and $Ne^{+\bullet} + C_{60}$, indicates that this novel *thermal-energy* process can compete effectively with dissociative charge-transfer channels, even when the latter channels are considerably more exothermic. We argue here that fragmentation of the target neutral is impeded by the robust nature of its cyclic structure and that this favors the loss of a second electron to form the observed dication. The observation of formation of $C_{10}H_8^{2+}$ from $He^{+\bullet}$ reacting with naphthalene at thermal energies has implications for the formation of PAH dications in interstellar clouds and circumstellar envelopes.

Introduction

Charge transfer is one of the most commonly observed processes in gas-phase ion–molecule chemistry. For thermalized reactants, one electron is transferred from the neutral to the reactant ion. The process of "double charge transfer" (DCT),[1] which has been used to investigate the second ionization potential of benzene[2] and other neutrals, involves collision between a kinetically excited ion and a neutral as indicated in reaction 1. The dication is

$$X^+ + Y \rightarrow Y^{2+} + X^- \qquad (1)$$

produced in the charge inversion of X^+ to X^-. Studies of DCT have generally used H^+, OH^+, and F^+ projectile ions because of the high ionization potential and/or electron affinity of $H^\bullet$, $OH^\bullet$, and $F^\bullet$. Production of the dication Y^{2+} is almost always endothermic and must be driven by the translational energy of the projectile.

A similar technique, with which the endothermicity of dication production is overcome by the translational energy of a projectile ion, is "charge stripping".[3] In this technique, the projectile ion is further ionized by collision with a neutral as shown in reaction 2. The second ionization potential of X can be determined by this process, by measuring the loss in kinetic energy of the projectile.

$$X^+ + Y \rightarrow X^{2+} + Y + e \qquad (2)$$

Dications can also be formed by electron-impact ionization and by photoionization. A recent review[4] has summarized techniques for generating and studying organic dications in the gas phase. An important subset of organic dications, those formed from aromatic compounds, is not covered by this review,[4] but dications of benzene[5-7] and larger aromatic compounds[7-15] have been extensively studied in mass-spectrometry experiments during the past 54 years. Of particular relevance to the present work are studies of the naphthalene dication generated by electron impact.[7,11,12] and threshold photoelectron–photoion coincidence.[16,17] The latter studies have indicated an enthalpy of formation for the d_8-naphthalene dication of 532 ± 12 kcal mol^{-1}, based on its appearance potential from $C_{10}D_8$.

The reaction of $He^{+\bullet}$ with naphthalene is of interest for its consequences in the chemistry of dense interstellar clouds.[18] Polycyclic aromatic hydrocarbons have been widely implicated as being responsible for observed spectroscopic features of interstellar space.[19-21] Omont[22] has suggested that the reaction of $He^{+\bullet}$ with polycyclic aromatic hydrocarbon molecules in such clouds may yield doubly-charged product ions owing to the exceptionally high recombination energy of $He^{+\bullet}$. The occurrence of such a process is of wider interest also, because of its novelty as a reaction type *at thermal energies* and because it allows the study of energy deposition leading to fragmentation at excess energies which are less than those accessible by other techniques more widely employed in the mass-spectrometric study of dications. Other examples of dication production from reactions of monocations with neutral molecules have been reported previously, but these processes have involved reactant ions possessing greater than thermal energy.[23,24] Very recently, we have observed that the reactions of thermalized $He^{+\bullet}$ and $Ne^{+\bullet}$ with buckminsterfullerene, C_{60}, produce C_{60}^{2+} in addition to $C_{60}^{+\bullet}$.[25] Fullerenes are also believed[21,26] to play a part within the models of interstellar and circumstellar chemistry. The implications of fullerene dication formation for such models also have been discussed.[27,28]

Experimental Section

The results reported here were obtained using a selected-ion flow tube (SIFT) which has been described previously.[29,30] Measurements were performed at a temperature of 294 ± 2 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. All reagent gases used were of research grade. $He^{+\bullet}$, $Ne^{+\bullet}$, and $Ar^{+\bullet}$ were formed by electron-impact ionization of the appropriate rare gas. $C_{10}H_8$ (obtained from Aldrich with a stated purity of 99%) was introduced into the flow tube by passage of helium carrier gas through a glass tube wadded at the ends with glass wool and containing a powdered sample of naphthalene. The helium/naphthalene vapor introduced in this manner contained < 1% (relative to $C_{10}H_8$ concentration) of any reactive contaminants as judged by $Ar^{+\bullet}$ chemical ionization. The same method was used to introduce a $He/C_{10}H_8$ mixture into the ion source but with the glass tube heated so as to facilitate naphthalene vaporization. The flow of naphthalene into the flow tube was calculated from the measured flow of helium through the glass sample tube, using the assumption that the gas after passage through the powdered $C_{10}H_8$ was saturated with naphthalene (P_{vap} = 0.17 Torr at 294 K). Rate coefficients reported here have an estimated uncertainty of ±40%. Because of the

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TABLE I: Ion–Molecule Reactions Involving $C_{10}H_8^{2+}$

reactants	products[a]		k_{obs}[b]	k_L[c]
$He^+ + C_{10}H_8$	m/z 64	[0.22]	4.0	4.8
	$C_{10}H_6^{+\bullet} + H_2$	[0.15]		
	$C_6H_3^+ + C_4H_5^\bullet$	[0.11]		
	$C_6H_5^+ + C_4H_3^\bullet$	[0.09]		
	$C_6H_4^{+\bullet} + C_4H_4$	[0.07]		
	$C_4H_3^+ + C_6H_5^\bullet$	[0.06]		
	$C_8H_5^+ + C_2H_3^\bullet$	[0.06]		
	$C_{10}H_7^+ + H^\bullet$	[0.06]		
	$C_3H_3^+ + C_7H_5^\bullet$	[0.04]		
	$C_{10}H_8^{+\bullet}$	[0.03]		
	$C_2H_3^+ + C_8H_5^\bullet$	[0.02]		
	$C_4H_4^{+\bullet} + C_6H_4$	[0.02]		
	$C_7H_5^+ + C_3H_3^\bullet$	[0.02]		
	other[d]	[0.05]		
$Ne^+ + C_{10}H_8$	$C_6H_4^{+\bullet} + C_4H_4$	[0.17]	2.1	2.3
	$C_6H_5^+ + C_4H_3^\bullet$	[0.17]		
	$C_8H_5^+ + C_2H_3^\bullet$	[0.12]		
	$C_{10}H_8^{+\bullet}$	[0.08]		
	$C_7H_5^+ + C_3H_3^\bullet$	[0.07]		
	$C_8H_6^{+\bullet} + C_2H_2$	[0.06]		
	$C_{10}H_6^{+\bullet} + H_2$	[0.06]		
	$C_{10}H_7^+ + H^\bullet$	[0.06]		
	$C_5H_3^+ + C_5H_5^\bullet$	[0.05]		
	$C_4H_4^{+\bullet} + C_6H_4$	[0.04]		
	$C_6H_6^{+\bullet} + C_4H_2$	[0.04]		
	$C_3H_3^+ + C_7H_5^\bullet$	[0.03]		
	other[e]	[0.05]		
$Ar^{+\bullet} + C_{10}H_8$	$C_{10}H_8^{+\bullet}$	[0.52]	1.35	1.7
	$C_{10}H_7^+ + H^\bullet$	[0.46]		
	$C_8H_6^{+\bullet} + C_2H_2$	[0.02]		
m/z 64 + H_2	none		<0.01	
m/z 64 + Xe	none		<0.01	

[a] Reaction products, excluding the rare-gas atom (He/Ne/Ar). Branching ratios are given in parentheses. [b] Observed reaction rate coefficient in units of 10^{-9} cm^3 molecule^{-1} s^{-1}, determined as described in the Experimental Section. [c] Langevin collision rate coefficient, calculated according to the method of Gioumousis and Stevenson,[31] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [d] Minor product channels (~1% or less) were also noted due to $C_3H_2^{+\bullet}$, $C_4H_2^{+\bullet}$, $C_5H_3^+$, $C_6H_6^{+\bullet}$, $C_7H_3^+$, and $C_8H_6^{+\bullet}$. [e] Minor product channels (~1% or less) were also noted due to $C_4H_3^+$, $C_6H_2^{+\bullet}$, $C_6H_3^+$, and m/z 64.

multiplicity of products observed for the reactions of $He^{+\bullet}$ and $Ne^{+\bullet}$ with $C_{10}H_8$, product ratios reported for these reactions have an estimated absolute uncertainty of ±0.05 (e.g., 0.12 ± 0.05) for those channels accounting for >10% of the total products; channels accounting for ≤10% of total products have a relative uncertainty of ±50% (e.g., 0.04 ± 0.02) ascribed to them. Product channels accounting for less than 2% of total products have been reported here but may correspond to products of reactions involving contaminants.

Results

The results obtained are detailed in Table I. Rate coefficients for all reactions involving neutral $C_{10}H_8$ were obtained from the data for low flows (<2.0 × 10^{16} molecules s^{-1}) of naphthalene, since these data consistently reflected a good degree of linearity and gave values very close to the collisional rate coefficients. At higher flows of helium/naphthalene vapor, the reactant ion signal was always observed to decay at a substantially slower rate: we attribute this "tailing" effect to unsaturation of the helium carrier gas with naphthalene at high gas flows, consistent with the shorter "residence time" of helium within the naphthalene column at these high flows.

In the reaction of $He^{+\bullet}$ with $C_{10}H_8$, the dominant product was observed to occur at m/z 64, corresponding to an empirical formula of $C_5H_4^+$. We ascribe this product signal to $C_{10}H_8^{2+}$ rather than to $C_5H_4^{+\bullet}$: a peak at m/z 64.5, with an abundance of approximately 10% of that observed at m/z 64, was also detected and is ascribed to $^{13}C^{12}C_9H_8^{2+}$. The observed abundance ratio for these two peaks is consistent with that expected for $C_{10}H_8^{2+}$ on the basis of the natural ^{13}C:^{12}C abundance ratio. Therefore, while we cannot exclude the possibility that *some* $C_5H_4^{+\bullet}$ is present also as a product of the reaction of $He^{+\bullet} + C_{10}H_8$, the observed I($m/z$ 64):I(m/z 64.5) abundance ratio suggests strongly that the proportion of $C_5H_4^{+\bullet}$ to $C_{10}H_8^{2+}$ in the observed m/z 64 product signal is very small. Fragmentation to produce $C_5H_4^{+\bullet} + C_5H_4$ (while still substantially more exothermic than production of $C_{10}H_8^{2+}$) is a much less exothermic channel than competing, and intuitively more attractive, fragmentation processes such as $C_8H_6^{+\bullet} + C_2H_2$ and $C_6H_4^{+\bullet} + C_4H_4$ (see Table II). Not only does production of $C_5H_4^{+\bullet}$ require the successive or concerted scission of three C–C bonds of the naphthalene structure, rather than cleavage of only two C–C bonds for almost any other conceivable fragmentation process, there is also no thermochemical advantage (i.e., exothermicity payoff) or high density of states to favor $C_5H_4^{+\bullet}$ formation over other fragmentation processes.

TABLE II: Enthalpy of Reaction for Processes of the Type $X^{+\bullet} + C_{10}H_8 \rightarrow$ Products, for X = He, Ne, and Ar, in Order of Decreasing Exothermicity

products[a]	$\Delta H°_{He}$[b]	$\Delta H°_{Ne}$[c]	$\Delta H°_{Ar}$[d]	obsd?[e]
$C_{10}H_8^{+\bullet}$	−379.2	−309.6	−175.7	yes
$C_{10}H_7^+ + H^\bullet$	−351.1[f]	−281.4	−147.6	yes
$C_{10}H_6^{+\bullet} + H_2$	−273.9	−204.2	−70.4	He, Ne
$C_8H_6^{+\bullet} + C_2H_2$	−272.1	−202.4	−68.6	yes
$C_6H_6^{+\bullet} + C_4H_2$	−264.5	−194.8	−61.0	He, Ne
$C_4H_2^{+\bullet} + C_6H_6$	−243.2	−173.5	−39.7	He
$C_7H_5^+ + C_3H_3^\bullet$	−239.9[g]	−170.2	−36.4	He, Ne
$C_4H_3^+ + C_6H_5^\bullet$	−230.5[h]	−160.9	−27.0	He, Ne
$C_8H_7^+ + C_2H^\bullet$	−229.3	−159.7	−25.8	no
$C_6H_4^{+\bullet} + C_4H_4$	−216.6	−147.0	−13.1	He, Ne
$C_7H_6^{+\bullet} + C_3H_2$	−213.9[i]	−144.3	−10.4	no
$C_2H_2^{+\bullet} + C_8H_6$	−212.3	−142.7	−8.87	no
$C_6H_5^+ + C_4H_3^\bullet$	−209.6[j]	−139.9	−6.1	He, Ne
$C_4H_4^{+\bullet} + C_6H_4$	−198.8	−129.1	+4.5	He, Ne
$C_3H_2^{+\bullet} + C_7H_6$	−194.0[k]	−124.2	+9.6	He
$C_5H_4^{+\bullet} + C_5H_4$	−186.3	−116.6	+17.2	Ne
$C_3H^+ + C_7H_7^\bullet$	−173.4	−103.7	+30.1	no
$C^{+\bullet} + C_9H_8$	−132.9	−63.3	+70.6	no
$C_{10}H_8^{2+}$ + e	−71.1 ± 12[l]	−1.5 ± 12	+132.4	He
$C_6H_5^+ + C_4H_3^+$ + e	−39.6	+30.1	+163.9	He?
$C_7H_5^+ + C_3H_3^+$ + e	−34.9[g]	+34.8	+168.6	He?
$C_8H_6^{2+} + C_2H_2$ + e	−25.0 ± 12[m]	+44.7	+178.5	He?

[a] Products, excluding X. [b] Enthalpy of reaction, in kcal mol^{-1}, for X = He. Unless otherwise noted, $\Delta H°$ is calculated for the lowest-energy isomer of the indicated species from ref 32. [c] Enthalpy of reaction for X = Ne. [d] Enthalpy of reaction for X = Ar. [e] Indicates whether this channel was detected for the reaction $X^+ + C_{10}H_8$. [f] Calculated using $\Delta H°_f$(products) = 10.92 eV.[16] [g] Calculated using $\Delta H°_f(C_7H_5^+)$ = 311 kcal mol^{-1}.[33] [h] Calculated using PA(C_4H_2) = 177 ± 1.5 kcal mol^{-1}.[34] [i] Calculated using $\Delta H°_f$(c-C_3H_2) = 114 ± 4 kcal mol^{-1}.[35] [j] Calculated using $\Delta H°_f(C_4H_3^\bullet)$ = 124 kcal mol^{-1}.[36] [k] Calculated using $\Delta H°_f$(c-$C_3H_2^{+\bullet}$) = 325 ± 4 kcal mol^{-1}.[35] [l] Calculated using AP($C_{10}H_8^{2+}$) = 21.5 ± 0.5 eV.[16] [m] Calculated using AP($C_8H_6^{2+} + C_2H_2$) = 23.5 ± 0.5 eV.[16]

It is of interest to note that the observed efficiency of dication production from $He^{+\bullet} + C_{10}H_8$ is higher than the efficiency of any $C_nH_m^+ + C_{10-n}H_{8-m}$ dissociative charge-transfer product channels, despite the much larger exothermicities for these latter product channels. This is presumably a consequence of a higher density of states for dication production than for any dissociative charge-transfer channel at the resonant energy of the reaction. In any event, since dication formation involves ejection of an electron rather than a much heavier atomic or molecular fragment (which often also requires cleavage of several distinct bonds), production of $C_{10}H_8^{2+}$ may well be the most efficient method of excess energy disposal available to the initial reaction product.

Figure 1 compares the types of product channels seen for the reactions of $Si^{+\bullet}$, D^+, $Ar^{+\bullet}$, $Ne^{+\bullet}$, and $He^{+\bullet}$ with $C_{10}H_8$. A clear trend toward greater fragmentation with increasing exothermicity of charge transfer is evident. The reactions of $Si^{+\bullet}$ and D^+ have been investigated separately.[37,18] Here we shall compare the reactions of $He^{+\bullet}$, $Ne^{+\bullet}$, and $Ar^{+\bullet}$ with $C_{10}H_8$. Charge transfer from $Ar^{+\bullet}$ is exothermic by 176 kcal mol^{-1} and results in negligible fragmentation of the carbon skeleton. (Apart from the channels recorded in Table I, a very small signal at m/z 78 ($C_6H_6^{+\bullet}$) was

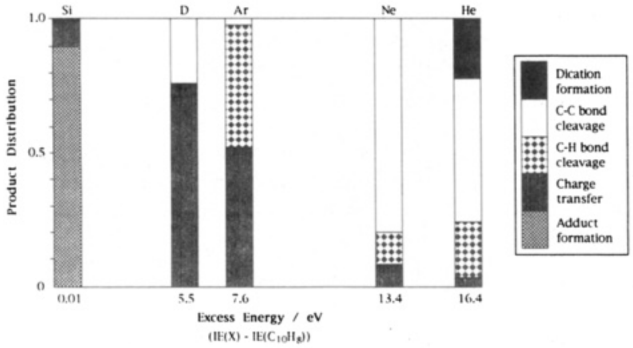

Figure 1. Bar graph showing product channels and distributions observed for reactions of atomic cations with naphthalene, $C_{10}H_8$, as a function of the exothermicity of charge transfer.

also detected, but was not included in the formal product assessment because it accounted for much less than 1% of the observed products. This signal may also arise from contaminant benzene adsorbed upon the powdered naphthalene surface.) Loss of a hydrogen atom from the ionized naphthalene appears to be the most accessible dissociation channel: all other fragmentations require at least two bonds to be broken. Charge exchange from $Ar^{+\bullet}$ to $C_{10}H_8$ has also been studied in a quadrupole ion trap: in the study of Brodbelt et al.,[38] a much higher degree of fragmentation to m/z 102 and 78 was reported than we have noted here. This is likely to reflect a difference in physical conditions and suggests that considerable excess energy was available to the reactants in the ion trap.

In the reaction with $Ne^{+\bullet}$, the exothermicity of charge transfer is substantially greater (310 kcal mol^{-1}), and loss of $H^\bullet$ from the charge-transfer product is still a significant channel; $C_{10}H_6^+$ formation (H_2 loss) is also noted. The apparent absence of $C_{10}H_6^{+\bullet}$ as a product from $Ar^{+\bullet}$ may reflect the greater difficulty of breaking two C–H bonds prior to rearrangement and is consistent with the very low yield of the similarly exothermic $C_8H_6^{+\bullet}$ + C_2H_2 channel from $Ar^{+\bullet}$. Fragmentation of the carbon skeleton dominates the $Ne^{+\bullet}$ product distribution, principally leading to the C_4, C_6, and C_8 ions which are thermochemically and/or kinetically favored. Some m/z 64 is observed, but this channel accounts for a mere 1% of the observed products and is considerably smaller than the neighboring signal at m/z 63. Production of the naphthalene dication from the reaction with $Ne^{+\bullet}$ is calculated to be exothermic by 1.5 ± 12 kcal mol^{-1}. Given the small intensity of the m/z 64 signal in this instance and the probability that dication production is endothermic, we attribute m/z 64 in this instance to the $C_5H_4^{+\bullet}$ ion; its low intensity is consistent with the difficulty, mentioned above, of rupturing three C–C bonds when rupture of two bonds allows access to more exothermic product channels. The very low intensity of the signal at m/z 64 in the reaction with $Ne^{+\bullet}$ suggests that the contribution of $C_5H_4^{+\bullet}$ to the m/z 64 signal in the reaction with $He^{+\bullet}$ is likely to be similarly low. This strengthens our assertion that the predominant component of m/z 64 from $He^{+\bullet}$ + $C_{10}H_8$ is the dication $C_{10}H_8^{2+}$.

Most major products from dissociative charge transfer from $Ne^{+\bullet}$ are also major products in the $He^{+\bullet}$ reaction, although m/z 78 and 102 are less abundant and m/z 51 is more abundant from $He^{+\bullet}$ than from $Ne^{+\bullet}$. We do not discount the possibility that some of the m/z 51 observed from $He^{+\bullet}$ is $C_8H_6^{2+}$, production of which is exothermic according to the observed appearance potential for this dication fragment from naphthalene, although we were not able to detect a signal at m/z 51.5 corresponding to the ^{13}C isotopomer of this dication. Other changes in the emphasis of products are also discernible in the product ratios from $He^{+\bullet}$ and $Ne^{+\bullet}$, which may reflect the possibility that some additional products result from dissociation of dications into two fragment ions. Charge separation (for example, formation of $C_6H_5^+$ + $C_4H_3^+$) in this manner would help to explain why closed-shell ions are more predominant from $He^{+\bullet}$ (70% of the total product ions) than from $Ne^{+\bullet}$ (52%), since fragmentation of a closed-shell dication to produce two closed-shell monocations generally should require less energy than fragmentation to produce two open-shell dications (such as $C_6H_4^{+\bullet}$ + $C_4H_4^{+\bullet}$). This should be identifiable by the "pairing" of product ratios for such charge separation product channels; the agreement between $He^{+\bullet}$ product ratios for $C_3H_3^+/C_7H_5^+$ (0.04:0.02), $C_4H_3^+/C_6H_5^+$ (0.06:0.09), $C_2H_3^+/C_8H_5^+$ (0.02:0.06), and $C_4H_5^+/C_6H_3^+$ (<0.01:0.11) is sometimes suggestive but not particularly convincing. Charge separation reactions may "boost" some of these observed product channels but do not appear to account for them entirely.

In an effort to investigate the reaction chemistry of $C_{10}H_8^{2+}$, we performed some studies of the subsequent reactivity of m/z 64 with reagent gases. Since m/z 64 was observed to react further with $C_{10}H_8$ (producing, we propose, either $C_{10}H_7^+$ + $C_{10}H_9^+$ or $C_{10}H_8^{+\bullet}$ + $C_{10}H_8^{+\bullet}$ by proton transfer or charge transfer: the occurrence of other secondary reactions prevented a unique identification) and since in any case it was not possible to add sufficient naphthalene to the flow tube to eliminate more than 90% of the reactant $He^{+\bullet}$, we restricted our initial studies to H_2 and to Xe since these gases display very low reactivity with $He^{+\bullet}$.[39] Several exothermic channels are possible for reaction of $C_{10}H_8^{2+}$ with H_2, and charge transfer to Xe is also exothermic for the dication. In practice, neither of these neutrals was observed to react with m/z 64. The failure of these neutrals to react with $C_{10}H_8^{2+}$, despite the existence of exothermic product channels, is not unexpected: such a lack of reactivity is a comparatively common finding in gas-phase dication chemistry owing to the existence of reverse activation energy barriers associated with charge separating reactions, arising from the Coulombic repulsion of monocationic product ions at close initial separations.[40,41] (This effect will also tend to disfavor the occurrence of charge separation product channels in the reaction of $He^{+\bullet}$ + $C_{10}H_8$, discussed above.)

Efforts were also made to inject m/z 64 into the flow tube from the ion source, using He saturated with $C_{10}H_8$ as the source gas. Electron bombardment of $C_{10}H_8$ and, we propose, the reaction of $He^{+\bullet}$ with $C_{10}H_8$ both produce $C_{10}H_8^{2+}$. Injection of m/z 64 was invariably accompanied by large contaminating signals at m/z 50, 51, 77, 78, and 128: these signals may arise from breakup of $C_{10}H_8^{2+}$ due to internal excitation, the kinetic energy imparted to the ions by the focusing electrostatic lenses in the ion source chamber, or by reaction of m/z 64 with impurities and naphthalene leaking from the ion source into the flow tube via the Venturi orifice. The ion at m/z 64 produced in this manner did not react with H_2, as was observed also for the m/z 64 product of the $He^{+\bullet}$ + $C_{10}H_8$ reaction and, additionally, was seen to charge transfer rapidly to C_6H_6 introduced into the tube, producing m/z 78. An ion with m/z 128 was also observed to increase as C_6H_6 was added, but this could arise through the reaction of contaminant $C_4H_3^+$ with C_6H_6.[42] Charge transfer from the lowest-energy isomer known of $C_5H_4^{+\bullet}$ to C_6H_6 is endothermic, so this reaction represents a possible diagnostic to distinguish between $C_5H_4^{+\bullet}$ and $C_{10}H_8^{2+}$.

Discussion

While only one previous observation of analogous thermal charge-transfer electron detachment processes has been reported,[25] it is interesting to note that the production of $C_{10}H_8^{2+}$ in the reaction of $He^{+\bullet}$ with $C_{10}H_8$ was foreshadowed not only by the suggestion of Omont[22] regarding the viability of such processes but also in the use of He II radiation, by Leach and co-workers,[16,17] to doubly ionize gas-phase naphthalene. We have now observed charge-transfer electron detachment reactions in three systems ($He^{+\bullet}$ + $C_{10}H_8$, $He^{+\bullet}$ + C_{60}, and $Ne^{+\bullet}$ + C_{60}): it therefore appears likely that this reaction channel is, where exothermic, not uncommon in the reactions of rare-gas cations with large aromatic molecules (and conceivably also with other neutral reagents). Further studies of the reaction chemistry of PAHs are in progress to investigate this notion.

Omont has argued that the production of dications in the reactions of $He^{+\bullet}$ with PAHs serves as a destruction mechanism for PAHs within the interstellar medium.[22] While it is true that the majority of product channels in this reaction are fragmentation channels leading, therefore, to a net reduction in molecular complexity of the products, it is by no means clear that dication production equates with subsequent fragmentation. In the reactions of $He^{+\bullet}$ and $Ne^{+\bullet}$ with C_{60},[25] dication formation occurs in the complete absence of fragmentation channels—a consequence of the unusually high cohesiveness of the fullerene carbon framework. Since planar PAHs inevitably have an "edge" and a multiplicity of available fragmentation channels involving cleavage of only one or two C–H or C–C bonds, they are somewhat less robust than fullerenes: nevertheless, the observation of $C_{10}H_8^{2+}$ as the largest observable product channel of the reaction of $He^{+\bullet}$ with naphthalene suggests that dication formation can occur without subsequent fragmentation. It is possible that quenching collisions with the helium buffer gas serve to stabilize the dications produced: if this is so, however, the dication initially produced must have a lifetime at least comparable with the time between collisions (on the order of 10^{-8} s) and more probably orders of magnitude in excess of this since He is a very poor quenching agent. This projected lifetime is several orders of magnitude higher than the likely vibrational frequency of any bonds within the excited dication, suggesting that, under conditions where an external quenching agent is absent, radiative stabilization of this species may compete effectively with dissociation.

The structure of the $C_{10}H_8^{2+}$ product discussed here is not known. However, the planar 10-membered-ring structure ascribed to $C_{10}H_8^{2+}$ by Leach et al.[17] has several benefits over other possible cyclic structures. Not only are the carbons bearing the positive charges as far apart as is possible for a 10-membered-ring system, but the charges are localized in in-plane orbitals that are diametrically opposed and hence serve to further isolate and separate the two charges. Finally, the 10π ring system is, according to the Hückel rule, aromatic and hence additionally stabilized. It remains to be seen, via detailed ab initio calculations, whether this structure is lower in energy than linear structures which would not be aromatic but which would benefit from considerably greater charge separation. It is likely, however, that the internal energy required to promote rearrangement to a linear structure is substantially higher than that required for formation of a cyclic structure, by analogy with the energies proposed by Jochims et al.[43] for the "low-energy" (bicyclic) and "high-energy" (acyclic) intermediates involved in the photoionization and subsequent fragmentation of naphthalene and azulene. The production of $C_{10}H_8^{2+}$ from $He^{+\bullet} + C_{10}H_8$ is exothermic by 71.1 kcal mol^{-1}, and this therefore represents an upper limit to the internal energy which can be partitioned into $C_{10}H_8^{2+}$ produced by this reaction. It is reasonable to expect that the extent of $C_{10}H_8^{2+}$ rearrangement occurring in the present experiments is less than that occurring in the bulk of mass-spectrometric studies of PAH dication formation and fragmentation, since these studies[5-15] use techniques (70-eV EI, etc.) which are likely to deposit substantially larger quantities of excess energy into the nascent dications.

Conclusion

The parent dication $C_{10}H_8^{2+}$ is seen to be the most abundant product of the reaction of $He^{+\bullet}$ with naphthalene. The production of this species is consistent with the expectation by Omont that such processes are viable[22] and with the occurrence of similar processes in the reactions of $He^{+\bullet}$ and $Ne^{+\bullet}$ with C_{60}.[25] Assignment of this product channel is complicated somewhat by the possibility of a signal due to $C_5H_4^{+\bullet}$ at the same mass-to-charge ratio: however, the signal due to $C_5H_4^{+\bullet}$ is a very minor product channel in the reaction of $Ne^{+\bullet}$ with naphthalene (where dication production appears to be endothermic), and the observed abundance of the ^{13}C isotopomer of $C_{10}H_8^{2+}$, at *m/z* 64.5, in the reaction with $He^{+\bullet}$ is consistent with the expected abundance. We shall discuss more fully elsewhere[18] the consequences of such dication formation with naphthalene, other PAHs, and fullerenes, for models of interstellar chemistry.

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References and Notes

(1) (a) Appell, J. In *Collision Spectroscopy*; Cooks, R. G., Ed.; Plenum Press: New York, 1978; p 244. (b) Fournier, P. G.; Fournier, J.; Salama, F.; Stark, D.; Peyerimhoff, S. D.; Eland, J. H. D. *Phys. Rev. A* **1986**, *34*, 1657.

(2) Griffiths, W. J.; Harris, F. M. *Chem. Phys.* **1991**, *157*, 299.

(3) Kemp, D. L.; Cooks, R. G. In *Collision Spectroscopy*; Cooks, R. G., Ed.; Plenum Press: New York, 1978; p 257.

(4) Lammertsma, K.; Schleyer, P. von R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321.

(5) Hustrulid, A.; Kusch, P.; Tate, J. T. *Phys. Rev.* **1938**, *54*, 1037.

(6) Wacks, M. E.; Dibeler, V. H. *J. Chem. Phys.* **1959**, *31*, 1557.

(7) Vekey, K.; Beynon, J. H.; Brenton, A. G. *Org. Mass Spectrom.* **1989**, *24*, 31.

(8) Higgins, W.; Jennings, K. R. *J. Chem. Soc., Chem. Commun.* **1965**, *99*, 97.

(9) Gallegos, E. J. *J. Phys. Chem.* **1968**, *72*, 3452.

(10) Ast, T.; Beynon, J. H.; Cooks, R. G. *Org. Mass Spectrom.* **1972**, *6*, 749.

(11) Engel, R.; Halpern, D.; Funk, B. A. *Org. Mass Spectrom.* **1973**, *7*, 177.

(12) Mathur, B. P.; Burgess, E. M.; Bostwick, D. E.; Moran, T. F. *Org. Mass Spectrom.* **1981**, *16*, 92.

(13) Kingston, R. G.; Guilhaus, M.; Brenton, A. G.; Beynon, J. H. *Org. Mass Spectrom.* **1985**, *20*, 406.

(14) Sim, P. G.; Jamieson, W. D.; Boyd, R. K. *Org. Mass Spectrom.* **1989**, *24*, 327.

(15) Pachuta, S. J.; Kenttämaa, H. I.; Sack, T. M.; Cerny, R. L.; Tomer, K. B.; Gross, M. L.; Pachuta, R. R.; Cooks, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 657.

(16) Ruhl, E.; Price, S. D.; Leach, S. *J. Phys. Chem.* **1989**, *93*, 6312.

(17) Leach, S.; Eland, J. H. D.; Price, S. D. *J. Phys. Chem.* **1989**, *93*, 7575; *J. Phys. Chem.* **1989**, *93*, 7583.

(18) Bohme, D. K.; et al. In preparation.

(19) *Polycyclic Aromatic Hydrocarbons and Astrophysics*; Léger, A., d'Hendecourt, L., Boccara, N., Eds.; Reidel: Dordrecht, 1987.

(20) Allamandola, L. J. *Top. Curr. Chem.* **1990**, *153*, 1.

(21) Bohme, D. K. *Chem. Rev.* **1992**, *92*, 1487.

(22) Omont, A. *Astron. Astrophys.* **1986**, *164*, 159.

(23) Horning, S. R.; Kotiaho, T.; Dejarme, L. E.; Wood, J. M.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *110*, 1.

(24) Wan, Z.; Christian, J. F.; Anderson, S. L. *J. Phys. Chem.* **1992**, *96*, 3344.

(25) Javahery, G.; Petrie, S.; Wang, J.; Bohme, D. K. *Chem. Phys. Lett.* **1992**, *195*, 7.

(26) Hare, J. P.; Kroto, H. W. *Acc. Chem. Res.* **1992**, *25*, 106.

(27) Petrie, S.; Javahery, G.; Bohme, D. K. *Astron. Astrophys.*, in press.

(28) Millar, T. J. *Mon. Not. R. Astron. Soc.* **1992**, *259*, 35p.

(29) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259.

(30) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *55*, 69.

(31) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

(32) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, supplement no. 1.

(33) Uggerud, E.; Arad, D.; Apeloig, Y.; Schwarz, H. *J. Chem. Soc., Chem. Commun.* **1989**, 1015.

(34) Petrie, S.; Knight, J. S.; Freeman, C. G.; Maclagan, R. G. A. R.; McEwan, M. J.; Sudkeaw, P. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *105*, 43.

(35) Clauberg, H.; Minsek, D. W.; Chen, P. *J. Am. Chem. Soc.* **1992**, *114*, 99.

(36) Ayranci, G.; Back, M. H. *Int. J. Chem. Kinet.* **1983**, *15*, 83.

(37) Bohme, D. K.; Wlodek, S.; Wincel, H. *J. Am. Chem. Soc.* **1991**, *113*, 6396.

(38) Brodbelt, J. S.; Louris, J. N.; Cooks, R. G. *Anal. Chem.* **1987**, *59*, 1278.

(39) Ikezoe, Y.; Matsuoka, S.; Takebe, M.; Viggiano, A. *Gas Phase Ion–Molecule Reaction Rate Constants Through 1986*; Ion Reaction Research Group Mass Spectrosc. Soc. Japan: Tokyo, Japan, 1987.

(40) Roth, L. M.; Freiser, B. S. *Mass Spectrom. Rev.* **1991**, *10*, 303.

(41) Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. *J. Phys. Chem.* **1992**, *96*, 6121.

(42) Lifshitz, C.; Reuben, B. G. *J. Chem. Phys.* **1969**, *50*, 951.

(43) Jochims, H. W.; Rasekh, H.; Rühl, E.; Baumgärtel, H.; Leach, S. *Chem. Phys.* **1992**, *168*, 159.