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Formation of $C_{10}H_8^+$ from the benzene radical cation: a case for the growth of polycyclic aromatic hydrocarbon ions by ion/molecule reactions in the gas phase?*

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ABSTRACT

Experimental results are reported which show that diacetylene, but not acetylene, adds rapidly to $C_6H_6^+$ in the gas phase in helium at 0.35 Torr and 296 ± 2 K when $C_6H_6^+$ is produced by the chemical ionisation of benzene with NO^+. The experiments were performed with the selected-ion flow tube and Fourier transform ion cyclotron resonance techniques. Chemical reactivity and ion photodissociation methods were employed to investigate the identity of the $C_{10}H_8^+$ ion produced by the addition reaction. Results were obtained for the reactions of this cation with deuterium, acetylene, diacetylene, styrene, trimethylamine, nitric oxide, 1,2,4,5-tetramethylbenzene and *p*-methylaniline, and were compared with the results of the reactions of these same molecules with the $C_{10}H_8^+$ radical cation produced directly from naphthalene by chemical ionisation with Si^+ and electron ionisation. Laser photodissociation experiments at 355 nm were also carried out on the $C_{10}H_8^+$ ion produced from the addition reaction, and by electron ionisation of naphthalene and azulene. The chemical and photophysical behavior of the former two ions was found to be identical which suggests that ionised naphthalene is formed in the addition reaction of ionised benzene and diacetylene. The implications of this result for the growth of polycyclic aromatic hydrocarbons in hydrocarbon flames and in interstellar regions are briefly discussed.

INTRODUCTION

Polycyclic aromatic hydrocarbon (PAH) molecules and ions seem to form under ionisation in a number of gaseous environments, both terrestrial and extraterrestrial. For example, neutral and positively-charged PAH molecules have been shown to be present in hydrocarbon flames in which they are perceived to act as intermediates in the formation of soot particles [1].

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* Dedicated to Professor Paul Kebarle on the occasion of his 65th birthday.

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Curiously, free PAH molecules and ions may also be present in interstellar regions in space which are much cooler and much less dense. Neutral and positively-charged fused-ring molecules such as pyrene, coronene and ovalene, either completely or partially hydrogenated, have been invoked to account for both the observed IR emission features in nebulae [2] and the observed diffuse interstellar absorption bands [3]. The very recent detection of additional sharp emission features [4] has led to the proposal that much simpler linear fused-ring molecules such as naphthalene, anthracene and tetracene are responsible for the IR emission [5]. For example, anthracene has been suggested as the most abundant of these linear polyacenes in the Orion Ridge [5]. Consequently there is a need to understand the chemistry of PAH ions and neutrals, particularly as regards to their growth in the gas phase at high and low temperatures and pressures. There has been considerable speculation in the scientific literature about such growth, but quantitative experimental measurements of the individual steps of growth are almost nonexistent. Here we report the results of an experimental study which is directed specifically toward the identification of ion/molecule reactions which may form naphthalene cations from benzene cations. Ionised naphthalene is the simplest ionic PAH. Its growth from benzene cations may serve as a prototype for analogous growth of larger PAH ions.

Growth of PAH ions or molecules can be envisaged to proceed in at least two different ways: either directly by cross-bonding in the side-on approach of extended chain-like molecules such as cumulenes or polyacetylenes (the inverse of the transformation of graphite at high temperatures) or through the successive build-up of hexagonal rings starting with benzene as the nucleus [6]. Both ionic and neutral versions of these mechanisms are possible. Laboratory measurements have already demonstrated the feasibility of forming benzene in the gas phase with ion/molecule reactions involving acyclic three carbon units. For example, formation of the benzenium ion (protonated benzene) has been shown to be possible in ionised allene and ionised propyne via the bimolecular reactions 1 and 2 [7]:

$$H_2C{=}C{=}CH_2^+ + H_2C{=}C{=}CH_2 \rightarrow C_6H_7^+ + H \tag{1}$$

$$HC{\equiv}C{-}CH_3^+ + HC{\equiv}C{-}CH_3 \rightarrow C_6H_7^+ + H \tag{2}$$

The benzenium ion may be neutralised to benzene by proton transfer or recombination with electrons:

$$C_6H_7^+ + M, e \rightarrow C_6H_6 + MH^+, H \tag{3}$$

$C_6H_6^+$ and $C_6H_7^+$ are also known to be formed from two carbon units in ionised acetylene by the successive addition of acetylene to $C_2H_2^+$ and $C_2H_3^+$ respectively, but the structures of the $C_6H_n^+$ ions which are formed in these cases have not been elucidated [6]. Neutralisation to benzene in this case would require electron transfer or proton transfer.

Here we explore the ability of acetylene and diacetylene to add to the benzene cation by ion/molecule reactions to form ionised naphthalene. We can imagine a two-step synthesis with acetylene, perhaps with ionised ethynylbenzene or ionised ethenylbenzene as intermediates, and a one-step synthesis with diacetylene. Chemical reactivity and ion photodissociation tests are used to determine whether any $C_{10}H_8^+$ produced is ionised naphthalene.

EXPERIMENTAL

All measurements of rate constants and product distributions were performed with the selected-ion flow tube (SIFT) apparatus in the Ion Chemistry Laboratory at York University which has been described in detail elsewhere [8,9]. Ions were formed either by electron impact in our usual manner with electron energies at around 75 eV, or by chemical ionisation. The latter option was chosen for the formation of $C_6H_6^+$ from benzene and $C_{10}H_8^+$ from naphthalene to minimise the possible internal energy content of these ions. NO^+ and Si^+ were found to have the appropriate electron recombination energies and were selected to achieve the charge transfer reactions 4 and 5:

$$NO^+ + C_6H_6 \rightarrow C_6H_6^+ + NO \qquad (4)$$

$$Si^+ + C_{10}H_8 \rightarrow C_{10}H_8^+ + Si \qquad (5)$$

in the flow tube upstream of the reaction region. The ionisation energies of NO (9.26436 ± 0.00006 eV), C_6H_6 (9.2459 ± 0.00002 eV), Si (8.15172 ± 0.00003 eV) and $C_{10}H_8$ (8.14 ± 0.01 eV) are such that reactions 4 and 5 are exothermic by only 0.018 and 0.01 ± 0.01 eV respectively [10]. Both charge transfer reactions were found to be sufficiently rapid to achieve the desired ionsiation and both were observed to proceed in competition with formation of adduct ions.

All the SIFT experiments were performed in helium carrier gas at about 0.35 Torr. No attempt was made to investigate the pressure dependence of rate constants and product distributions. Traces of water vapor in the helium buffer gas were removed by passing the buffer gas through a zeolite molecular sieve at 77 K. The reactant gases D_2, C_2H_2, NO, and trimethylamine (all Matheson) had minimum purities of 99.5, 99.6, 99.0 and 99.0% respectively. The diacetylene was prepared by the alkaline hydrolysis of 1,4-dichlorobut-2-yne and was stored at dry ice temperature to avoid polymerisation. Experiments with H_3^+ as "chemical ionisation" reagent indicated a purity of greater than 99%. Benzene and styrene (both Aldrich) were used as their vapors, diluted with helium as 10 mol% and 5 mol% mixtures respectively.

Confirmatory charge transfer and photodissociation experiments were carried out on a home-built (FT-ICR) mass spectrometer at the University of Florida equipped with a 2 T superconducting magnet and a 2.54 cm cubic cell, controlled by a Nicolet FTMS-1000 electronics console (now available from Extrel; more detail about this home-built vacuum system, including a figure, can be found in ref. 11). This system has been customised to allow the introduction of laser light into any of three laser windows on the source side or two windows on the solids inlet flange, and is equipped with two pulsed valves (General Valve Corp., Model 9-181-900) for sample introduction in addition to two standard leak valves.

In all FT-ICR experiments ions with frequencies from 10 kHz to 2.667 MHz were excited and 25–50 time domain signals (depending on signal strength) containing 16 k data points were averaged. The time domain signal was apodised using a modified Blackman–Harris window function [12] and zero-filled once prior to Fourier transformation. A 2 V trapping potential was used; lower voltages resulted in decreased trapping efficiency. Ions were formed by 12 eV electron ionisation in all experiments. The FT-ICR approach has been described in detail previously [13–15]. The chemicals used were high grade and subjected to several freeze–pump–thaw cycles before use. Purity was checked by looking at the FT-ICR spectrum and no untoward peaks were observed.

The frequency tripled output (355 nm) of a Quantel Nd : YAG laser (Model 581C, now available from Continuum) was used for ion photodissociation. The beam entered the vacuum chamber through one of the windows shown in Fig. 1 of ref. 11, was turned near the FT-ICR analyser cell by a quartz prism, entered the cell via a 1 cm diameter hole in an excite plate, made a single pass through the cell and exited through a 1 cm hole in the opposite excite plate in a manner similar to that shown for the "cw-CO_2 laser beam" in Fig. 1 of ref. 16. Estimated energy per pulse (pulse width ≈ 8 ns) incident on the trapped ions was 50 mJ in a beam of ≈ 1 cm diameter.

RESULTS

Reactions with $C_6H_6^+$ cations

The rate constants and products determined with the SIFT apparatus for the reactions of $C_6H_6{}^+$ cations derived from benzene by charge transfer with NO^+ are summarised in Table 1.

$C_6H_6{}^+$ did not react with acetylene with a measurable rate, $k \leqslant 4 \times 10^{-13}\,\mathrm{cm}^3$ molecule^{-1} s^{-1}, irrespective of whether it was produced by electron impact or chemical ionisation. Available enthalpies of formation [10] indicate that the elimination of molecular hydrogen to form ionised ethynylbenzene according to

$$C_6H_6^+ + C_2H_2 \rightarrow C_6H_5C_2H^+ + H_2 \qquad (6)$$

TABLE 1

Summary of rate constants ($10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$), reaction efficiencies and products determined for reactions of $C_6H_6^+$ radical cations produced from benzene by chemical ionisation with NO^+ at 296 ± 2 K

Reaction[a]	k_{exp}[b]	k_{exp}/k_c[c]
$C_6H_6^+ + D_2 \rightarrow$ no reaction	$\leqslant 0.0002$	$\leqslant 0.0002$
$C_6H_6^+ + C_2H_2 \rightarrow$ no reaction	$\leqslant 0.0004$	$\leqslant 0.0004$
$C_6H_6^+ + C_4H_2 \rightarrow C_{10}H_8^+$	0.5	0.5
$C_6H_6^+ + C_6H_6 \rightarrow C_{12}H_{12}^+$	> 0.05	> 0.04
$C_6H_6^+ + C_8H_8 \rightarrow C_8H_8^+ + C_6H_6$	0.78	0.5

[a] C_6H_6 and C_8H_8 represent the vapors of benzene and styrene respectively.

[b] The effective bimolecular rate constant is given at a total helium pressure of 0.35 Torr and a helium density of 1.15×10^{16} atoms cm^{-3}. The accuracy of the rate constants is estimated to be better than ±30%.

[c] k_{exp}/k_c is a measure of reaction efficiency. Collision rate constants, k_c, are derived from the combined variational transition state theory–classical trajectory study of T. Su and W.J. Chesnavich, J. Chem. Phys., 76 (1982) 5183.

is $5\,kcal\,mol^{-1}$ exothermic so that it might be expected to occur. Several addition reactions to form an isomer of $C_8H_8^+$ such as ionised ethenylbenzene, for example, are also exothermic. But there was no evidence for the formation of such products, not even the formation of an adduct ion, perhaps weakly bound by electrostatic interaction. Also, there was no evidence for the formation of $C_8H_7^+$ by H-atom elimination.

In sharp contrast to the reaction with acetylene, $C_6H_6^+$ was found to add diacetylene at close to the collision rate! The effective bimolecular rate constant for reaction 7:

$$C_6H_6^+ + C_4H_2 \rightarrow C_{10}H_8^+ \tag{7}$$

in helium buffer gas at 0.34 Torr was measured to be $5.0 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$ which is within a factor of two of the collision rate constant (see Table 1).

The counter-reaction of ionised diacetylene (produced by electron impact at 75 eV) with neutral benzene was observed in separate experiments to proceed rapidly and predominantly by charge transfer as shown in reaction 8:

$$C_4H_2^+ + C_6H_6 \rightarrow C_6H_6^+ + C_4H_2 \tag{8}$$

The rate constant for this reaction was found to be $1.0 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$. The charge transfer is exothermic by 0.933 eV in this case since the ionisation energy of diacetylene is 10.1080 ± 0.003 eV. Up to 5% of the reaction could have proceeded by proton transfer since $C_6H_7^+$ was observed to be formed, but the source of this ion could not be identified unambiguously. The adduct ion was also observed to be formed, but only in trace amounts, $\leqslant 2\%$. The $C_6H_6^+$ ion was observed to react further with benzene to form the ionised dimer with an effective bimolecular rate constant $\geqslant 5 \times 10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ in helium at 0.345 Torr.

We can also report that ionised benzene does not react with deuterium, $k \leqslant 2 \times 10^{-13}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. Neither D-atom transfer, reaction 9, nor D-atom exchange, reaction 10

$$C_6H_6^+ + D_2 \rightarrow C_6H_6D^+ + D \tag{9}$$

$$C_6H_6^+ + D_2 \rightarrow C_6H_5D^+ + HD \tag{10}$$

were observed to occur. H-atom transfer can be computed to be endothermic by 23 kcal mol^{-1} from the known enthalpies of formation of $C_6H_6^+$ and $C_6H_7^+$ [10].

$C_6H_6^+$ was also observed to transfer a charge to styrene, $k = 7.8 \times 10^{-10}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. This charge transfer reaction is exothermic by 0.82 eV.

Reactions with $C_{10}H_8^+$ cations

SIFT results

The high efficiency established for the addition reaction of $C_6H_6^+$ with diacetylene suggests the presence of strong chemical bonding in the $C_{10}H_8^+$ adduct ion which could mean that the adduct ion is ionised naphthalene. This possibility was tested chemically in two ways. First, the reactivity of $C_{10}H_8^+$ derived from the addition reaction was compared with that of $C_{10}H_8^+$ produced by the direct ionisation of naphthalene. Charge transfer was chosen as the probe reaction and trimethylamine and styrene as the electron-donor molecules. Trimethylamine and styrene have ionisation energies of 7.82 ± 0.06 and 8.43 ± 0.06 eV respectively, and closely bracket the ionisation energy of naphthalene, 8.14 ± 0.1 eV [10]. Second, the $C_{10}H_8^+$ ion derived from the addition reaction was reacted with NO. If diacetylene is weakly bound to $C_6H_6^+$ it should be displaced by NO in a "switching" reaction of type 11 leading to covalently-bound protonated nitrosobenzene:

$$C_6H_6^+ \cdot C_4H_2 + NO \rightarrow (C_6H_6NO)^+ + C_4H_2 \tag{11}$$

Thermochemical data for the enthalpy of dissociation of protonated nitrosobenzene into $C_6H_6 + NO^+$ and $C_6H_6^+ + NO$ indicate values of 46.1 and 46.0 kcal mol^{-1} respectively [10]. We can therefore expect reaction 11 to occur if $D(C_6H_6^+ \cdot C_4H_2) < 46\,\mathrm{kcal\,mol^{-1}}$. Reents and Freiser [17] have observed the addition of NO^+ to C_6H_6 for which they have determined a binding energy of 45.9 kcal mol^{-1} which is consistent with formation of protonated nitrosobenzene.

Table 1 shows that $C_{10}H_8^+$ ions were observed to react in an identical fashion whether they were produced by the chemical reaction 7 or from

TABLE 2

Summary of rate constants (10^{-9} cm^3 molecule^{-1} s^{-1}), reaction efficiencies and products determined for the reactions of $C_{10}H_8^+$ cations derived (a) by ionisation of naphthalene or (b) from the association of ionised benzene with diacetylene at 296 ± 2 K

Reaction[a]	k_b		k_{exp}/k_c^c
	(a)	(b)	
$C_{10}H_8^+ + D_2 \rightarrow$ no reaction	$\leqslant 0.0004$	$\leqslant 0.0004$	$\leqslant 0.0004$
$C_{10}H_8^+ + C_2H_2 \rightarrow$ no reaction	$\leqslant 0.001$	$\leqslant 0.001$	$\leqslant 0.001$
$C_{10}H_8^+ + C_4H_2 \rightarrow C_{14}H_{10}^+$	$\leqslant 0.001$	$\leqslant 0.001$	$\leqslant 0.001$
$C_{10}H_8^+ + C_8H_8 \rightarrow$ no reaction	$\leqslant 0.001$	$\leqslant 0.001$	$\leqslant 0.0007$
$C_{10}H_8^+ + (CH_3)_3N \xrightarrow{0.8(0.7)} (CH_3)_3N^+ + C_{10}H_8$	1.1	1.0	1.0
$\xrightarrow{0.2(0.3)} (CH_3)_3NH^+ + C_{10}H_7$			
$C_{10}H_8^+ + NO \rightarrow$ no reaction	$\leqslant 0.0002$	$\leqslant 0.0002$	$\leqslant 0.0003$

[a] C_8H_8 represents the vapor of styrene. The product distributions are rounded off to the nearest 5% and are estimated to be accurate to within ±30%.

[b] The effective bimolecular rate constant is given at a total helium pressure of 0.35 Torr and a helium density of 1.15×10^{16} atoms cm^{-3}. The accuracy of the rate constants is estimated to be better than ±30%.

[c] k_{exp}/k_c is a measure of the reaction efficiency. Collision rate constants, k_c, are derived from the combined variational transition state theory–classical trajectory study of T. Su and W.J. Chesnavich, J. Chem. Phys., 76 (1982) 5183.

naphthalene by the charge-transfer reaction 5. They were observed not to react with styrene, $k \leqslant 10^{-12}$ cm^3 molecule^{-1} s^{-1}, but fast reactions were observed with trimethylamine with the channels indicated in reaction 12

$$C_{10}H_8^+ + (CH_3)_3N \rightarrow (CH_3)_3N^+ + C_{10}H_8 \qquad (12a)$$

$$\rightarrow (CH_3)_3NH^+ + C_{10}H_7 \qquad (12b)$$

which correspond to charge and proton transfer. Rate constants of 1.0 and 1.1×10^{-9} cm^3 molecule^{-1} s^{-1} and branching ratios of 0.7/0.3 and 0.8/0.2 were obtained for the chemically-formed adduct and the ionised naphthalene respectively. These results all agree within the experimental uncertainty of the measurements and so suggest that the chemically-formed adduct is ionised naphthalene. Furthermore, a loosely-bound adduct ion with $D(C_6H_6^+ \cdot C_4H_2) > 19$ kcal mol^{-1}, as required by the failure to observe charge transfer with styrene, could not lead to the proton transfer channel observed with trimethylamine which is endothermic with $D(C_6H_6^+ \cdot C_4H_2) > 13.5$ kcal mol^{-1}.

No reaction was observed with NO, $k < 2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This observation argues against the chemically-formed $C_{10}H_8^+$ ion being a weakly-bound adduct ion with $D(C_6H_6^+ \cdot C_4H_2) < 46$ kcal mol^{-1}.

Also, no reactions were observed with deuterium, $k \leqslant 4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. D-atom transfer, reaction 13, and D-atom exchange, reaction 14

$$C_{10}H_8^+ + D_2 \rightarrow C_{10}H_8D^+ + D \qquad (13)$$

$$C_{10}H_8^+ + D_2 \rightarrow C_{10}H_7D^+ + HD \qquad (14)$$

did not occur. Available enthalpies of formation and the proton affinity of naphthalene indicate that H-atom transfer is endothermic by 34 kcal mol^{-1} [10]. While this result does not provide structural information, it is of interest for the chemistry of interstellar clouds which can be rich in molecular hydrogen.

The $C_{10}H_8^+$ ions were found to be unreactive with C_2H_2, $k \leqslant 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. It is interesting to note that when electron impact was used to generate $C_{10}H_8^+$ from naphthalene a small fraction, < 5%, of the $C_{10}H_8^+$ was observed to react rapidly with acetylene in the manner shown in reaction 15:

$$(C_{10}H_8^+)^* + C_2H_2 \rightarrow C_{12}H_9^+ + H \qquad (15)$$

This H-atom elimination reaction was attributed to an excited form of $C_{10}H_8^+$. No such reaction was observed when $C_{10}H_8^+$ was created by reactions 5 and 7 in which much less excess energy is available for excitation.

A further reaction of $C_{10}H_8^+$ with C_4H_2 to form $C_{14}H_{10}^+$ was observed to occur, but at a much slower rate, $k \leqslant 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, than the addition of the first C_4H_2 molecule to $C_6H_6^+$.

FT-ICR results

FT-ICR studies of $C_{10}H_8^+$ reactivity also employed charge transfer reactions of these ions with 1,2,4,5-tetramethyl benzene (IE = 8.04 eV) and *p*-methylaniline (IE = 7.24 eV) [10]. Because of the high rate of charge transfer of $C_4H_2^+$ with C_6H_6, experiments which formed $C_{10}H_8^+$ began with ionisation of benzene alone, followed by introduction of diacetylene via a pulsed valve after the end of the electron beam pulse. Thus no $C_4H_2^+$ ions could be formed by electron ionisation, and $C_{10}H_8^+$ ions were produced only via reaction 7. The benzene ion reacted almost completely and there was no evidence for other ions being formed by fragmentation of the adduct. Following ejection of any unreacted $C_6H_6^+$ ions from the FT-ICR cell, a second pulsed valve was then used to introduce either 1,2,4,5-tetramethylbenzene of *p*-methylaniline. The $C_{10}H_8^+$ ions produced via reaction 7 readily charge exchanged with these two charge transfer agents, as did $C_{10}H_8^+$ ions produced by electron ionisation of naphthalene. However, $C_{10}H_8^+$ ions produced by electron ionisation of azulene (IE = 7.41 eV, [10]), were unreactive with 1,2,4,5-tetramethylbenzene and underwent charge transfer to a lesser extent with *p*-methylaniline than did the $C_{10}H_8^+$ ions produced by the other two methods.

In separate experiments diacetylene was introduced continuously at a lower pressure rather than admitting it via the pulsed valve in order to estimate the rate constant. $C_4H_2^+$ ions were ejected during the electron beam time to prevent them from producing $C_6H_6^+$ by charge transfer during the time of reaction. The rate constant obtained at a pressure of about 10^{-6} Torr was about 1×10^{-10} cm^3 molecule^{-1}s^{-1} which is somewhat less than measured at the much higher pressures of the SIFT experiments, but still quite large.

Photodissociation of $C_{10}H_8^+$ cations

The 355 nm photodissociation behavior of the $C_{10}H_8^+$ ion formed by the reaction of benzene cations with diacetylene was compared to that of the $C_{10}H_8^+$ ion formed by electron ionisation of naphthalene and azulene. Results are shown in Fig. 1. The irradiation wavelength was chosen to coincide with an allowed transition "f–g" between the highest occupied and lowest unoccupied Π orbitals of the naphthalene cation [18–19[a]]. In photodissociation studies involving the $C_{10}H_8^+$ ion/molecule reaction product, any unreacted $C_6H_6^+$ ions were ejected from the cell, so that the *m/z* 128 ion was the only ion present at the time of laser irradiation. When naphthalene and azulene were ionised by 12 eV electrons, only *m/z* 128 ions were observed and these were subjected to the 355 nm light. Identical experimental conditions were employed for naphthalene and azulene photodissociation experiments.

The photodissociation behaviors seen for the adduct ion produced in the $C_6H_6^+ + C_4H_2$ reaction and for the $C_{10}H_8^+$ ion produced from naphthalene were identical. The major product ion was seen at *m/z* 102 and corresponds to $C_8H_6^+$ produced by loss of acetylene from the parent ion. Minor products were observed at *m/z* 39, 50, 51, 63, 74, 126, and 127. The photodissociation spectrum observed for the $C_{10}H_8^+$ ion produced from azulene differed from that of the other two by the additional appearance of peaks at *m/z* 76, 77, and 78, and a reduced intensity of the *m/z* 126 peak. A partial explanation for the different spectrum of azulene can be found in a consideration of the photodissociation energetics. A photon of wavelength 355 nm possesses an energy equivalent to 80.5 kcal mol^{-1}. The photodissociation pathways observed for $C_{10}H_8^+$, regardless of how it was produced, all require more than this amount of energy. Indeed, the absorption of two or more photons by the $C_{10}H_8^+$ ion is required to cause dissociation. For example, the major dissociation which was observed, loss of C_2H_2 to form $C_8H_6^+$, is endoergic by 90 kcal mol^{-1} for azulene cations, and by 106 kcal mol^{-1} for naphthalene cations [10]. One possible explanation for the enhanced abundance of *m/z* 76 ions in the photodissociation spectrum of azulene parent ions versus that in the spectra of naphthalene parent ions and $C_{10}H_8^+$ ions formed via reaction 7, is that the most stable forms of the $C_6H_4^+$ ion (*m/z* 76) and C_4H_4 molecule can be formed from azulene$^+$ by absorption of only two 355 nm photons

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[a] A solid state absorption spectrum of the naphthalene cation is reproduced in Fig. 3 of ref. 19.

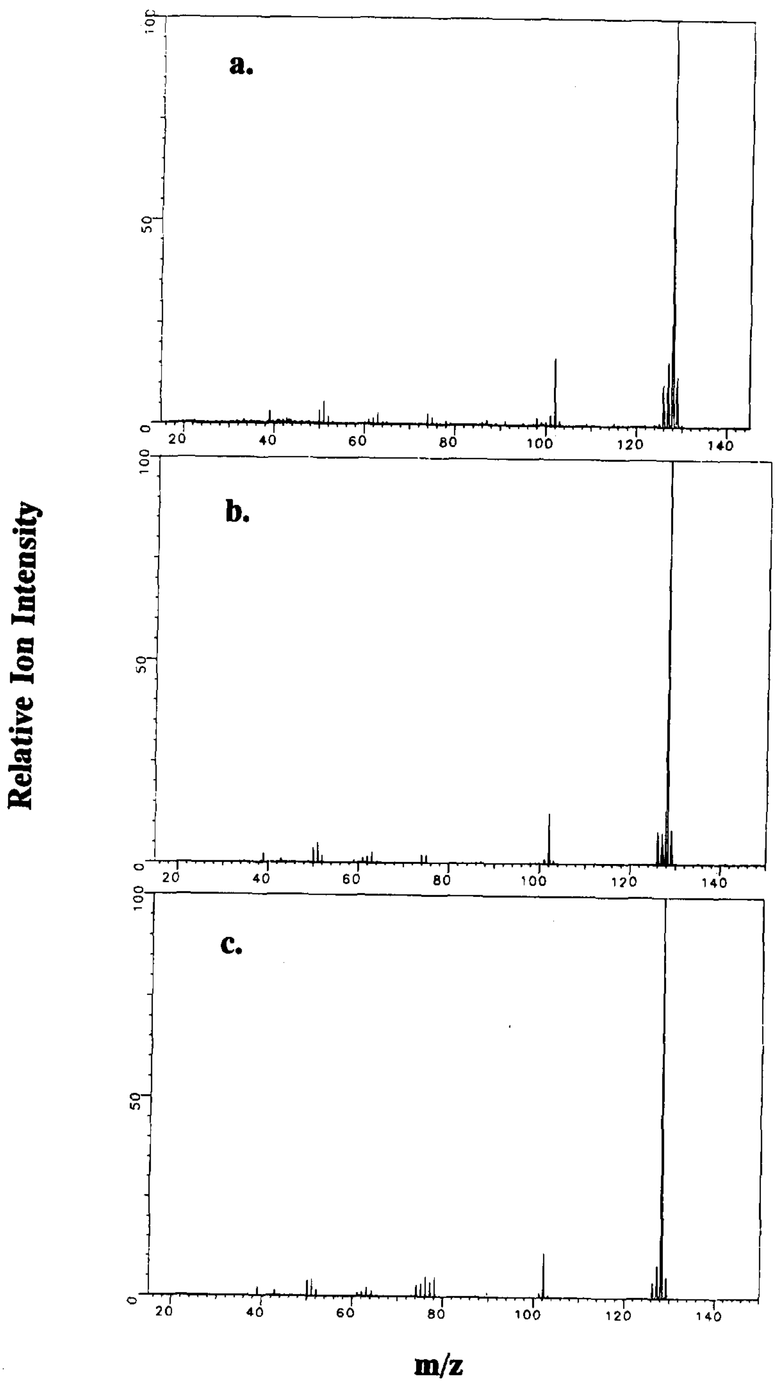

Fig. 1. Photodissociation spectra (355 nm) of $C_{10}H_8^+$ ions: (a) ions formed by the reaction $C_6H_6^+ + C_4H_2$; (b) ions formed by electron ionisation of naphthalene; (c) ions formed by electron ionisation of azulene. Other conditions are as described in the text.

(146 kcal mol^{-1} [10]), while absorption of three 355 nm photons (162 kcal mol^{-1} [10]) is needed to form this particular ion and neutral pair from naphthalene$^+$. A similar argument holds for the formation of the phenyl cation and the C_4H_3 neutral from azulene$^+$ for which about 149 kcal mol^{-1} is required compared with the 165 kcal mol^{-1} required for the formation of these species from naphthalene$^+$ [10]. The reason for the enhancement of *m/z* 78 and the decrease in *m/z* 126 is not understood.

DISCUSSION

With only 0.018 eV of excess energy, the chemical ionisation of benzene by NO^+ can be expected to leave the benzene structure intact and to result in the formation of the benzene radical cation in the SIFT experiments. Furthermore, the numerous collisions which this ion undergoes with helium atoms before entering the reaction region should ensure that the benzene radical cations are also thermalised to the temperature of the helium carrier gas. The SIFT measurements show clearly that benzene radical cations produced in this way add rapidly to diacetylene in helium carrier gas at 0.34 Torr and 296 ± 2 K. The addition is remarkably efficient, occurring in one of every two collisions. In sharp contrast, the addition reaction with acetylene proceeds with a rate more than 1000 times slower under the same conditions. The large rate constant and high efficiency obtained for the diacetylene addition reaction, together with the observed failure of the "switching" reaction of the adduct with nitric oxide, provide compelling evidence for the formation of a stable product ion involving covalent bonding. Formation of essentially all of the possible covalently-bonded isomers of $C_{10}H_8^+$ is expected to be exothermic. For example, we may note that available enthalpies of formation indicate that the addition of diacetylene to benzene ions to form ionised naphthalene is exothermic by 115 kcal mol^{-1} [10]. Now we need to ask which of these isomers is (are) formed preferentially.

There are, of course, many isomers of $C_{10}H_8^+$. Unfortunately, the enthalpies of formation of only a very few have been characterised in the gas phase so far. The recent compilation of Lias et al. [10] lists only the ions of naphvalene, azulene and naphthalene, of which the naphthalene ion is the most stable. Other bicyclic isomers, e.g. ionised 1-methylene-1-*H*-indene (benzofulvene) or 2-methylene-2-*H*-indene (isobenzofulvene), and several substituted monocyclic isomers are also possible, but little is known about them or even the corresponding neutral parent molecules. Only a few of the neutral isomers of $C_{10}H_8$ have been successfully synthesised so far and often not in the absence of other isomers such as naphthalene which appears to be the most stable [20–22]. Given this sparsity of information on enthalpies of formation, we cannot rely on thermochemistry to provide a means for discriminating between the various possibilities.

Can mechanistic considerations help? At least three types of bonding need to be considered: acyclic addition leading to substituted benzene ions; cycloadditions of the Diels–Alder type; and additions of C_4H_2 across the ring. [2 + 2], [2 + 3] and [2 + 4] additions would lead to ionised 1-vinyl-benzocyclobutadiene, 1-methylene indene and naphthalene respectively. Of these, the cycloaddition to form ionised naphthalene may be favored, relatively speaking, since it demands the least amount of shifting of hydrogen atoms. [4 + 2], [4 + 3] and [4 + 4] additions of C_4H_2 across the $C_6H_6^+$ ring may lead to three-dimensional structures for the adduct ion. There is no a priori reason for preferring any one of these three types of bonding in the adduct ion. We may suggest, however, that if cycloaddition is preferred, formation of ionised naphthalene may be favored.

Molecular orbital considerations can provide a plausible mechanism for the formation of ionised naphthalene as follows. During the initial interaction pi-coordination with one of the triple bonds of diacetylene (with donation/back-donation) leads to the weakening of the triple bond. This may be followed by sigma-bonding to a carbon atom of the benzene ring with syn-orientation of the second triple bond. This promotes additional pi-stabilisation via intramolecular pi-interaction with benzene (again with donation/back-donation), again with weakening and polarisation of the triple bond. Ab initio calculations by Wu and Houk [23] have shown that such a transition state in the syn-configuration is energetically more favorable than the corresponding anti-configuration. From this syn-configuration, 1,2-addition to the benzene ring becomes favored in view of the possible rotations about the two single bonds of "diacetylene", in view of the alteration of charge in the benzene ring which leads to a coulombic gradient which favors the 2-position [24], and in view of the lengthening of the 1,2-C–C bond in benzene as a result of a change in hybridisation from sp^2 to sp^3 at the 2-position. This mechanistic path allows formation of a new 1,6-C–C bond and ultimately stabilisation resulting in formation of the naphthalene ion.

It is also of interest to note previous results of an experimental study of the addition of 1,3-butadiene to the benzene cation reported by Holman et al. [25]. The addition was observed in the high-pressure source (0.1–0.7 Torr) of a tandem mass spectrometer in a 1 : 1 mixture of benzene and 1,3-butadiene ionised by electron impact. Collision-assisted decomposition (CAD) spectra were used to provide structural information. A two-step mechanism involving the initial formation of a 2-phenyl-2-butene cation which subsequently ring-closes to the 1-methylindan cation was proposed on the basis of closely matching CAD spectra at high and low pressures (low and high energies respectively). Other possibilities which were ruled out, without direct comparisons of CAD spectra however, were the [2 + 4] cycloaddition to form bicyclo[4.4.0.]deca-2,4,8-triene cation, the [2 + 2] addition to form 7-vynyl-bicyclo[4.2.0]octa-2,4-diene, and the [4 + 2] addition to form 7-vinyl-bicyclo [2.2.2]octa-2,5-diene. The extent to which this study of the 1,3-butadiene addition provides an analogy for our study of the addition reaction with diacetylene is questionable since our experiments were performed with ground-state $C_6H_6^+$ cations and involved a different adduct molecule, but the methodology of the 1,3-butadiene investigation is instructive.

Chemical reactivity and ion photodissociation rather than CAD were employed in this study as probes for structure. In principle, the unambiguous identificiation of the $C_{10}H_8^+$ adduct ions by any of these methods would require the systematic investigation of the reactions of all of the possible isomeric ions of $C_{10}H_8^+$. This is clearly not practical. For the most part the neutral isomers are difficult or impossible to synthesise in a pure form, as already indicated. Their ionisation energies and enthalpies of formation are almost completely unknown, as are the chemical ionisation charge-transfer reactions which might be required to selectively produce the structurally intact ion. In the SIFT experiments we have focused instead on a comparative reactivity study with ionised naphthalene since this is likely to be the most stable isomer of $C_{10}H_8^+$ and so likely to be favored as the product in the addition reaction. In the FT-ICR experiments both naphthalene and azulene were used in the comparative ion-photodissociation and charge-transfer studies.

The SIFT charge-transfer bracketing experiments with styrene and trimethylamine establish a window for the ionisation energy of the $C_{10}H_8$ species produced in the addition reaction between 7.82 and 8.43 eV. The ionisation energy of naphthalene, 8.14 eV, falls within this window as may that of naphvalene, (IE = 8.0 eV [10]). The ionisation energy of azulene, 7.41 eV [10]), falls outside, as may that of 1-methylene indene if it is significantly lower than that of indene (IE = 8.14 eV [10]).

The FT-ICR charge transfer experiments reinforce and improve on the SIFT results in that the observation of the charge transfer reaction of the adduct ion with 1,2,4,5-tetramethyl benzene decreases the width of the window to between 8.04 and 8.43 eV. The FT-ICR results also clearly exclude the possibility of formation of ionised azulene as, of course, is required by this window. On the basis of these results it seems that the $C_{10}H_8^+$ produced by the addition reaction might well be ionised naphthalene.

The proposal that the observed adduct ion $C_{10}H_8^+$ is ionised naphthalene becomes more credible when the SIFT results of the comparative reactivity test with trimethylamine are considered. There is agreement, within experimental error, both in the total rate constants for reaction and, more significantly, in the product distributions for the charge and proton transfer reaction channels. We would expect the product distribution especially to be sensitive to the isomeric structure of $C_{10}H_8^+$ in which case this result alone should provide compelling evidence for the formation of ionised naphthalene.

Finally, the ion photodissociation results are also consistent with the assignment of the naphthalene structure to the product $C_{10}H_8^+$ of the addition reaction of $C_6H_6^+$ with C_4H_2 as the photodissociation behavior of this ion is identical to that of $C_{10}H_8^+$ produced from naphthalene by electron impact.

The failure of acetylene to react with benzene ions in the SIFT experiments is curious. The bimolecular product channel leading to the formation of ionised ethynylbenzene by the elimination of H_2 is exothermic by 12 kcal mol^{-1} but was not observed to occur. Also, although the addition reaction to form ionised ethenylbenzene (styrene) is itself exothermic by 58 kcal mol^{-1} and other addition reactions to form $C_8H_8^+$ isomers are also substantially exothermic, no addition reactions were observed to occur. Apparently activation energies are operative or, in the case of the addition reactions, lifetimes for collisional or radiative stabilisation are unfavorable for their rapid occurrence at room temperature. Our experiments show unequivocally that direct growth by addition of diacetylene is preferred over sequential growth by reactions with acetylene. The high rate of addition of diacetylene may also be surprising in view of its high excess energy (115 kcal mol^{-1}) which must be disposed. But the exeriments show that of all of this exothermicity is accommodated without significant fragmentation of the $C_{10}H_8^+$ ion, either to bimolecular products or back to reactants, under the conditions of both the SIFT and the FT-ICR experiments, although there is much less chance for collisional stabilisation in the latter. The high rate observed under FT-ICR conditions may imply that the adduct is extremely long-lived and that radiative stabilisation is quite important. Indeed, the guidelines for the efficiency of radiative association reactions proposed by Dunbar [26] on the basis of his calculations suggest an efficiency at a temperature around 300 K close to one for the formation of $C_{10}H_8^+$ for which the number of internal degrees of freedom, N is 48 and the binding energy is 5 eV. Also, because the efficiency of radiative association is predicted to be extremely sensitive to binding energy, the Dunbar guidelines suggest a much lower efficiency of less than 0.01 for the association reaction with acetylene to form ionised ethenylbenzene for which N is 46 and the binding energy is 2.5 eV.

As for the further growth of the naphthalene cation, it is interesting to note that some addition of diacetylene to the naphthalene cation was observed in the SIFT experiments but at a much slower rate (more than 500 times slower) than that for addition to the benzene cation. In contrast, acetylene and styrene were observed not to add to the naphthalene ion at all. These results imply that further addition of diacetylene to form anthracene or phenanthrene cations may be possible but with a much reduced rate, at least at room temperature. At flame temperatures or in hot circumstellar envelopes these higher-order addition reactions may well be more facile.

Current opinions on the production and loss of interstellar PAHs have recently been reviewed by Turner [27] who indicates that PAHs are probably formed mostly in the hot, dense envelopes of evolved stars from which they are ejected into the interstellar medium. Perhaps they also become incorporated into hydrogenated amorphous carbon surfaces as proposed by Duley and Jones [5] or condense to form larger graphitic grain particles. Unsaturated hydrocarbon chain molecules are known to be present in circumstellar envelopes and methylacetylene is a known interstellar molecule [27]. Although association reactions in the interstellar medium must take place radiatively because of the low density, collisional association becomes possible in dense circumstellar envelopes [16]. It is therefore conceivable that association reactions of the type identified by reactions 1 and 2 proceed to form benzene ions and that further reactions with diacetylene contribute to the formation of PAH ions in these envelopes. Also one may speculate that this chemistry is not fundamentally dissimilar to that leading to PAH ions in fuel-rich hydrocarbon flames which develop soot particles.

The observation that diacetylene and not acetylene adds to the benzene cation may have implications for analogous neutral reactions. Little is known about the onset of the gas-phase production of PAH molecules by neutral reactions. The current state of our knowledge has recently been surveyed by Frenklach and Feigelson [28] in a numerical kinetic investigation of the likely chemistry in carbon-rich circumstellar envelopes. The chemistry was adopted from studies of soot production in hydrocarbon pyrolysis and combustion. It is activated by H-atom abstraction rather than ionisation and is restricted to acetylene addition as the dominant mechanism of carbon growth. For example, growth of naphthalene from benzyne is construed to occur via the following reaction sequence:

$$C_6H_4 \xrightarrow{+H} C_6H_5^{\cdot} \xrightarrow[(-H)]{C_2H_2} C_6H_5C_2H \xrightarrow[(-H_2)]{+H} C_6H_4C_2H^{\cdot} \xrightarrow{C_2H_2} C_{10}H_7^{\cdot} \qquad (16)$$

There are essentially no experimental data or theoretical calculations available for these reactions. While the results reported here for ionic reactions are not directly relevant to the neutral scheme presented in eqn. 16, they do point towards the possibility of a significant uncertainty in the kinetics of the acetylene chemistry and to the potential importance of diacetylene chemistry which was not considered by Frencklach and Feigelson [28]. For example, we now need to ask whether $C_6H_5^{\cdot}$ cannot directly react with diacetylene and whether such a one-step synthesis for $C_{10}H_7^{\cdot}$ is preferred to the three-step mechanism given in reaction 16.

Clearly the data base for the kinetics of individual reactions important in the growth of PAH molecules by either neutral or ion chemistry is still severely limited. Here we have shown that some of this data may now be in reach, at least for ions. However, the many possible isomeric variations make the task a difficult one. To make the task more manageable at York University, we are currently in the process of adding an ion trap to our SIFT mass spectrometer in order to make available the structural information which can be provided by collision-induced dissociation experiments.

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