C—N bond formation in the reaction of nitrogen ions N$^+$ with benzene molecules

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Abstract

We have investigated the ring-opening reaction of N$^+$(^{3}P) ions with benzene in a guided ion beam tandem mass spectrometer under single collision conditions. Our attention is focussed on the mechanisms by which C—N bonds are formed. We have measured the kinetic energy dependence of the integral cross-section for the reaction channels leading to the formation of H$_2$CN$^+$, H$_2$C$_2$N$^+$, H$_2$C$_3$N$^+$, H$_3$C$_4$N$^+$, HC$_5$N$^+$ and H$_2$C$_5$N$^+$. The present work indicates that the title ion molecule reaction represents a potential route to form cyano molecules from aromatic hydrocarbons, and thus may be relevant for the production of molecules of biological interest in the interstellar space. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Aromatic and polyaromatic molecules are known to be present in extraterrestrial matter such as carbon stars, molecular clouds and meteorites; their presence has been observed in astronomical spectra [1–3], and the recent observation of benzene in interstellar space [4] has aroused further interest in the chemical behaviour of the entire class of molecules for the modelling of astrophysical processes. Given the relevance of molecules containing carbon and nitrogen atoms in such context, an understanding of mechanisms by which C—N bonds might be formed from C—C chain or ring reactants should provide insights into the possible astrophysical origin of life's building blocks [5,6].

To this end, much attention has recently been devoted to studying the growth of complex molecules containing C—N bonds. Several reaction mechanisms have been proposed including the reaction of CN radicals with unsaturated hydrocarbons [7–9], and the aggregation of cyanoacetylene, which may be catalysed by doubly charged PAH or fullerene cations [10]. In this Letter, we investigate another possible pathway based on the reaction of N$^+$ with benzene. This was suggested by the observation that the nitrogen ion is isoelectronic with the neutral carbon atom, whose insertion into a benzene ring has recently been observed both experimentally [11] and computationally [12] to form, under single collision conditions, the seven-membered ring C$_7$H$_5$ radical. The reaction of C$^+$ ions with benzene has been studied in the past [13,14] providing the first evidence of a C$_7$H$_5^+$ intermediate. We report here the observation of product ions such as cyanoallene CH$_2$CCHCN$^+$, cyanopolyacetylenes HC$_5$N$^+$ and HC$_5$NH$^+$, as

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well as lighter compounds such as H_2CN^+ and $H_2C_2N^+$. Our results indicate that aromatic hydrocarbons can be directly converted into cyano and amino molecules, thus giving a complementary pathway to the reaction mechanisms mentioned above.

2. Experimental

Our experimental apparatus, shown in Fig. 1, is a guided ion beam tandem mass spectrometer that has been described previously [15]. Nitrogen ions, produced by electron impact of N_2 in a differentially pumped ion source, are mass-selected by a magnetic mass spectrometer and subsequently injected into a radio-frequency octopole ion guide [16] which passes through the reaction cell containing benzene at about 10^{-5} mbar. Reactant and product ions are extracted from the octopole, analysed by a quadrupole mass spectrometer, and finally detected by an electron multiplier. The axial energy distribution of the N^+ beam, determined by using the octopole guide as a retarding field energy analyser, typically shows a full width at half maximum of about 0.6 eV. The collision energy in the laboratory frame is varied by changing the potential difference between the octopole and the ion source, and at each collision energy the relative
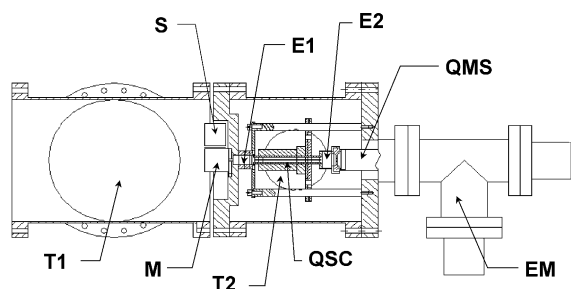

Fig. 1. Schematic view of the experimental set-up: two vacuum chambers are differentially pumped by turbomolecular pumps (T1) and (T2). The first chamber houses the ion source (S) and the magnetic sector mass spectrometer (M). The ion beam is focussed by an Einzel lens (E1) into the second chamber which contains the octopole ion guide surrounded by the scattering cell (QSC). Ionic reactants and products are collected by a second set of ion optics (E2) and guided into the quadrupole mass spectrometer (QMS). Finally, ions are counted by an electron multiplier (EM).

integral cross-section is derived from the ratio between the product and reactant count rates [17]. To minimize the production of N^+ in electronically excited states (^1D and ^1S), the source pressure of N_2 has been kept as high as possible to favour quenching of the excited states. For the same reason the electron energy has been lowered down to $\sim$40 eV and ion focussing potentials have been carefully controlled. Even if the presence of a small fraction of excited N^+ ions cannot be completely ruled out, we expect that it does not significantly affect our measurements [18].

A major problem in our experiment is originated by the presence of the intense and rich spectrum due to the dissociative ionisation of benzene. For example, the signal due to $H_2C_5N^+$ which appears in the mass spectrum at a mass–charge ratio $m/q = 76$ is completely hidden by the more intense $C_6H_4^+$ signal at the same m/q ratio. To extract the signal of interest, we therefore use a suitable combination of isotopically labelled reactants, $^{15}N^+$ and C_6D_6. Pure hexadeuterated benzene yields a fragmentation pattern that is dominated by a sequence of peaks, with a spacing of two atomic mass units (a.m.u.) and lying at even masses; there is also a small contribution from $C_nH_m^+$ fragments containing a ^{13}C carbon atom, whose effect can be eliminated knowing the natural abundance of ^{13}C. Thus, the reaction of C_6D_6 with $^{15}N^+$ ions leading to C—N bond formation yields peaks at odd masses which are shifted by 1 a.m.u. when the primary ion beam is switched from $^{14}N^+$ to $^{15}N^+$. Moreover, the combination of measurements using C_6D_6 or C_6H_6 and $^{14}N^+/^{15}N^+$ provides information about signal backgrounds and makes possible a cross-check of the experimental results. A typical mass spectrum is shown in Fig. 2.

3. Results and discussion

The reaction of N^+ with benzene has recently been the subject of a detailed investigation by Arnold et al. [19] using a flow tube apparatus. The most abundant ionic product at 300 K was found to be $C_6H_6^+$, while several other ionic products of the form $C_nH_m^+$ resulted from dissociative charge transfer. While C—N bond formation was
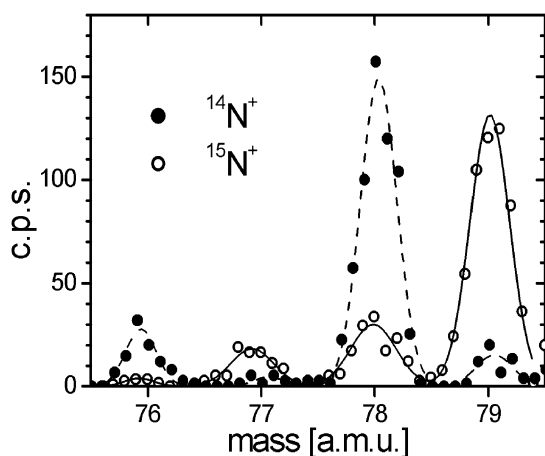
Fig. 2. Typical mass spectra of products from collisions of $^{14}N^+$ and $^{15}N^+$ ions with C_6D_6 at a relative collision energy ~ 2.5 eV. N-containing products at m/q ratios equal to 76 and 77 correspond to DC_5N^+ ions while signals at $m/q = 78$ and 79 relate to the product $D_2C_5N^+$. Solid and dashed lines correspond to Gaussian fits of the experimental peaks for $^{15}N^+$ and $^{14}N^+$, respectively.

suggested for neutral products including HCN and CH_2CN, it was concluded that ionic products were limited to those containing only carbon and hydrogen.

In our experiment, we have concentrated on the production of ions containing C—N bonds and, by using a more sensitive guided ion beam apparatus, we have been able to detect the species H_2CN^+, $H_2C_2N^+$, $H_2C_3N^+$, $H_3C_4N^+$, HC_5N^+ and $H_2C_5N^+$. Despite the high sensitivity of our experimental apparatus, we have not been able to observe production of $C_6NH_5^+$, which would correspond to the insertion products C_7H_5 and $C_7H_5^+$ observed in the reaction with neutral [11] and ionic [14] carbon, respectively.

Results for the production of N-containing fragments measured using $^{15}N^+$ and both C_6H_6 and C_6D_6 are presented in Fig. 3 as a function of the collision energy in the centre of mass frame. Along the ordinate axis we give absolute cross-sections in Å^2 that have been estimated by comparison with the charge transfer channel for production of $C_6H_6^+$, the latter being calibrated using measured rate constant values [19] with an absolute uncertainty of $\pm 50\%$. Whereas absolute cross-sections thus determined are somewhat un-
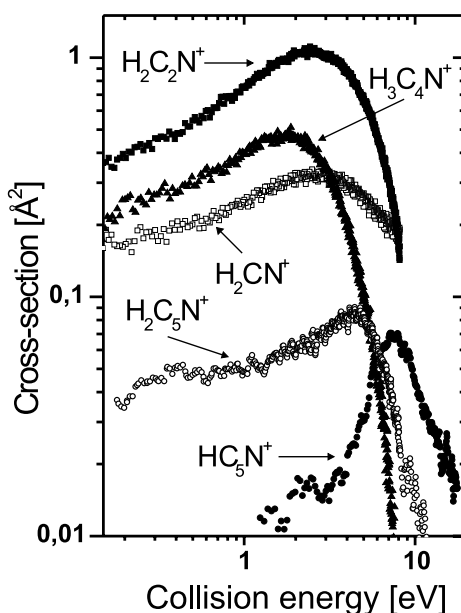

Fig. 3. Reactive integral cross-sections for the production of H_2CN^+, $H_2C_2N^+$, $H_3C_4N^+$, HC_5N^+ and $H_2C_5N^+$ from the reaction of $^{15}N^+$ with C_6H_6/C_6D_6 as a function of the centre of mass collision energy in the range 0.2–10 eV. Cross-sections for $H_2C_3N^+$ are not shown but are of the same order of magnitude as for H_2CN^+. The data are valid for both isotopes of hydrogen.
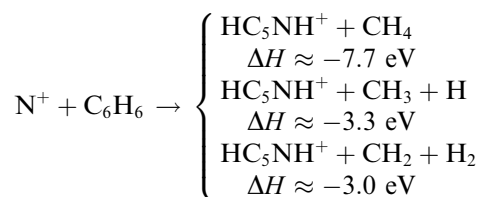
certain, relative values are much more precise. Data for formation of $H_2C_3N^+$ have not been shown in Fig. 3 because they are affected by larger errors, but an estimate gives a cross-section of the same order of magnitude as that for the production of H_2CN^+.

Although we make no direct determination of the neutral partners formed at the same time as the detected ionic species, we are able to deduce, at least in part, the contributing reaction channels from analysis of the measured energy dependence of the reactive integral cross-sections. In the absence of dynamical barriers along the potential energy surface connecting reactants to products, exoergic processes are characterized by a non-zero cross-section at low collision energy, while the presence of a threshold in the cross-section is the signature of either an endoergic process or a barrier on the route to an exoergic reaction. When the heats of formation ($\Delta_f H^\circ$) of reactants and products are well known, thermodynamic thresholds

can easily be calculated and compared with experimental values. For the larger ionic products observed in this work, $\Delta_f H°$ are unfortunately not known, and we therefore resort to very preliminary density functional calculations (B3LYP/cc-pVTZ) [20] of the reaction energetics performed by Osamura [21]. More accurate calculations of the potential energy surfaces involved in the reactions, which take into account the possible presence of barriers and the geometry of transition states, are in progress.

3.1. $H_2C_5N^+$ and HC_5N^+

The cross-section for formation of $H_2C_5N^+$ rises gently from a value around 0.04 Å^2 at low energies until a sharp descent follows the peak around 5 eV. The most stable structure of $H_2C_5N^+$ is calculated to be linear protonated cyanopolyacetylene $H-C\equiv C-C\equiv C-C\equiv NH^+$ in the singlet state, while a triplet state is a few eV higher in energy. From calculations of the reaction energetics [21] and the energy dependence of the experimental cross-section, we infer that both exoergic and endoergic channels could contribute to product formation in the collision energy range explored by our experiment. The relevant exoergic channels for formation of HC_5NH^+ in the singlet state include:

$$N^+ + C_6H_6 \rightarrow \begin{cases} HC_5NH^+ + CH_4 \\ \quad \Delta H \approx -7.7 \text{ eV} \\ HC_5NH^+ + CH_3 + H \\ \quad \Delta H \approx -3.3 \text{ eV} \\ HC_5NH^+ + CH_2 + H_2 \\ \quad \Delta H \approx -3.0 \text{ eV} \end{cases}$$
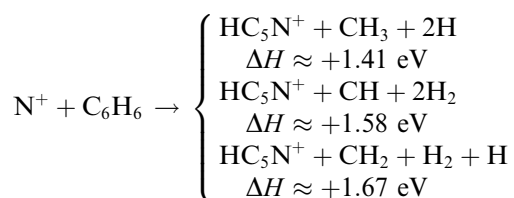
while analogous channels leading to HC_5NH^+ in the triplet state are still slightly exothermic. Endoergic channels of interest for our experiment include the formation of singlet HC_5NH^+ together with $C + 2H_2$, $CH_2 + 2H$ and $CH + H_2 + H$. Thresholds for such channels range from about 0.5 to 1.5 eV. Further measurements, concerning in particular the distribution of the kinetic and internal energy of ionic products, would be necessary to distinguish between these channels.

As shown in Fig. 3, the cross-section for the reaction $N^+ + C_6H_6 \rightarrow HC_5N^+ +$ neutral rises

from below 0.01 Å^2 at energies below a probable threshold around 1 eV to reach a maximum an order of magnitude higher at 7–8 eV. Several product channels may contribute. The linear cyanopolyacetylene cation $HCCCCCN^+$ is calculated to be the most stable form of HC_5N^+ [21] and, provided that there are no large barriers on the route to exoergic products, the negligible cross-section that we measure at low collision energies permits us to rule out the exoergic channels which yield $HC_5N^+ + CH_4 + H$ ($\Delta H \approx -3.01$ eV) and $HC_5N^+ + CH_3 + H_2$ ($\Delta H \approx -3.09$ eV).

Amongst the endoergic channels, those showing the lowest thresholds are the following:

$$N^+ + C_6H_6 \rightarrow \begin{cases} HC_5N^+ + CH_3 + 2H \\ \quad \Delta H \approx +1.41 \text{ eV} \\ HC_5N^+ + CH + 2H_2 \\ \quad \Delta H \approx +1.58 \text{ eV} \\ HC_5N^+ + CH_2 + H_2 + H \\ \quad \Delta H \approx +1.67 \text{ eV} \end{cases}$$

while all other channels have much higher thresholds (above 5–6 eV). On this basis, any of the three above-mentioned channels can contribute to the production of HC_5N^+ at lower collision energies (i.e. $\leqslant 5$–6 eV).
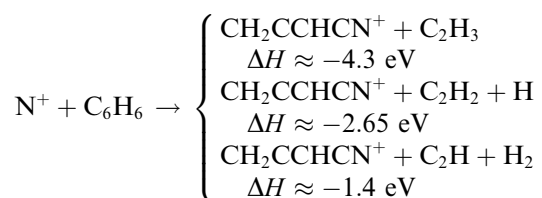
We note that the sharp increase in the cross-section for formation of HC_5N^+ occurs in the same energy region as that in which the $H_2C_5N^+$ signal declines, the maxima of the two reaction channels being separated by ~2.5 eV. This suggests that HC_5N^+ might be produced by loss of an H atom from $H_2C_5N^+$ and in this case we could rule out contribution from the channel leading to $HC_5N^+ + CH + 2H_2$.

3.2. $H_3C_4N^+$

The neutral species H_3C_4N was observed by Lee and co-workers [8] as a product of the reaction of the cyano radical CN with methylacetylene CH_3CCH. The ionic species, as well as the neutral, can exist in two different isomers, the cyanopropyne ion $CH_3-C\equiv C-CN^+$ and the cyanoallene ion $CH_2=C=CH-CN^+$, and the latter is predicted to be the more stable form by ~0.6 eV. The cross-section we measure for production of the $H_3C_4N^+$ ion shows a gentle monotonic in-

crease from 0.2 Å^2 at low energies towards a maximum at about 2 eV, followed by a sharp descent. As the first endoergic channel ($CH_2CCHCN^+ + C_2H + H + H$) has been estimated to have a threshold at about 3 eV, we discard contributions from endoergic channels and ascribe the rise in cross-section to the formation of exoergic products in increasingly excited ro-vibrational states. An alternative explanation, which cannot be eliminated without calculation of the potential energy surface involved in the reactive channels, would be the presence of energy barriers.
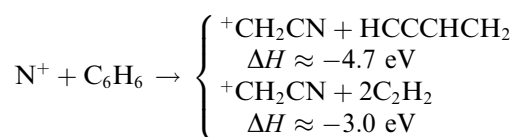
The enthalpies of reaction for the following three exoergic channels have been calculated [21]:
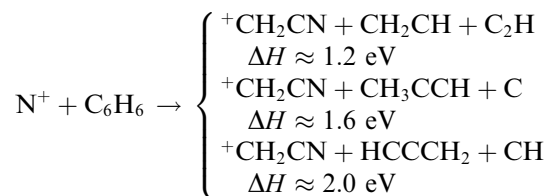
$$N^+ + C_6H_6 \rightarrow \begin{cases} CH_2CCHCN^+ + C_2H_3 \\ \quad \Delta H \approx -4.3 \text{ eV} \\ CH_2CCHCN^+ + C_2H_2 + H \\ \quad \Delta H \approx -2.65 \text{ eV} \\ CH_2CCHCN^+ + C_2H + H_2 \\ \quad \Delta H \approx -1.4 \text{ eV} \end{cases}$$

We conclude that the ion CH_2CCHCN^+ could be produced via any or all of these channels, and that a significant contribution from endoergic processes would not be expected, at least in the low collision energy range. Endoergic channels may open up, along with the formation of products in internally excited states, as the collision energy is increased.

3.3. $H_2C_2N^+$

The $H_2C_2N^+$ ion is the most abundant N-containing reaction product (see Fig. 3). The measured cross-section shows a monotonic increase from 0.4 Å^2 at low energies towards a maximum between 2 and 3 eV, followed by a sharp descent. The thermochemistry of the various reaction channels leading to the cyanomethylene ion $^+CH_2$—$C\equiv N$ has been evaluated from a published value for its heat of formation, $\Delta_f H^\circ = 12.6$ eV [22]. The exoergic channels which might contribute to our signal, in the low collision energy range, are found to be the following:
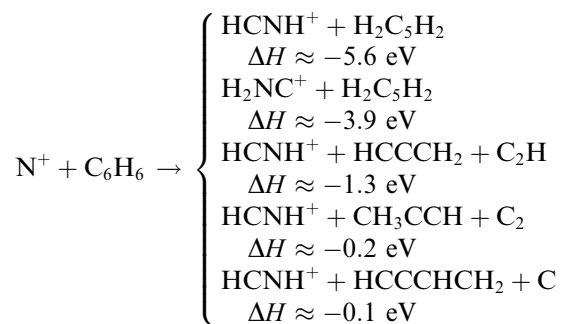
$$N^+ + C_6H_6 \rightarrow \begin{cases} {}^+CH_2CN + HCCCHCH_2 \\ \quad \Delta H \approx -4.7 \text{ eV} \\ {}^+CH_2CN + 2C_2H_2 \\ \quad \Delta H \approx -3.0 \text{ eV} \end{cases}$$

Although experimental data show no evidence of a threshold, endoergic channels such as:

$$N^+ + C_6H_6 \rightarrow \begin{cases} {}^+CH_2CN + CH_2CH + C_2H \\ \quad \Delta H \approx 1.2 \text{ eV} \\ {}^+CH_2CN + CH_3CCH + C \\ \quad \Delta H \approx 1.6 \text{ eV} \\ {}^+CH_2CN + HCCCH_2 + CH \\ \quad \Delta H \approx 2.0 \text{ eV} \end{cases}$$

may contribute at higher collision energies.

3.4. H_2CN^+

The cross-section for production of H_2CN^+ (see Fig. 3) shows a very gentle, monotonic increase up to a maximum of 0.3 Å^2 at about 3 eV and falls less rapidly at high collision energies than the cross-sections for the other channels discussed so far. Starting from a published value for the heat of formation of the most stable isomer $HC\equiv NH^+$ ($\Delta_f H^\circ = 9.8$ eV [22]), we estimate the thermochemistry of the various reaction channels. The isomeric form H_2NC^+ lies ~1.7 eV [22] higher in energy than $HC\equiv NH^+$, so that the exoergic channels relevant to the present study are the following:

$$N^+ + C_6H_6 \rightarrow \begin{cases} HCNH^+ + H_2C_5H_2 \\ \quad \Delta H \approx -5.6 \text{ eV} \\ H_2NC^+ + H_2C_5H_2 \\ \quad \Delta H \approx -3.9 \text{ eV} \\ HCNH^+ + HCCCH_2 + C_2H \\ \quad \Delta H \approx -1.3 \text{ eV} \\ HCNH^+ + CH_3CCH + C_2 \\ \quad \Delta H \approx -0.2 \text{ eV} \\ HCNH^+ + HCCCHCH_2 + C \\ \quad \Delta H \approx -0.1 \text{ eV} \end{cases}$$

Any or all of these channels could contribute to production of H_2CN^+ ions.

4. Conclusion

Our experimental investigation of the reaction of the N^+ ion with benzene, supported by preliminary calculations of the reaction energetics, has demonstrated the production of C—N containing species such as $HCNH^+$, H_2CCN^+,

$H_2C_3N^+$, CH_2CCHCN^+, HC_5NH^+ and HC_5N^+ via channels which involve a degree of chemical rearrangement by allowing the rupture of C—C and the formation of C—N bonds. The cross-sections for these processes are $\sim$10–1000 times smaller than those for charge-transfer yielding $C_6H_6^+$ and N. The present work indicates that ion-molecule processes can convert aromatic hydrocarbons into cyano molecules, the building blocks of amino acids, and thus may be involved in the chemical routes to molecular complexity. Further experiments particularly designed to probe structures and kinetic/internal energy distributions of ionic products, will be necessary for a deeper understanding of the dynamics of such systems.

Acknowledgements

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