Mass spectrometric studies of azides: reactions of Ar$^+$ with 3-azidopropionitrile, 2-azidopropionitrile, and azidoacetonitrile in a Fourier transform ion cyclotron resonance mass spectrometer

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Abstract

The reactions of Ar$^+$ with 3-azidopropionitrile, 2-azidopropionitrile, and azidoacetonitrile have been studied in a Fourier transform ion cyclotron resonance mass spectrometer. The dominant and, in the case of 2-azidopropionitrile the only, primary reaction is charge transfer although the resultant molecular ion immediately fragments. In the cases of 3-azidopropionitrile and azidoacetonitrile a small amount of hydrogen abstraction to form ArH$^+$ occurs. In addition to the unambiguous identification of the molecular formula of the product ions leading in most cases to suggested chemical structures with known proton affinities, the time profiles of the product ions were determined and kinetic analysis allowed the primary product ions to be differentiated from the secondary product ions. Many secondary reactions of the primary ions with the parent neutral molecule occur, the majority initiated by proton transfer. Some of them lead to fragmentation but others to the protonated azidonitrile. A comparison with a recently published account of the EI fragmentation of the same three azidonitriles leads to the suggestion that Ar$^+$ chemical ionisation is potentially more appropriate for investigating the decomposition of fragile molecules such as the azidonitriles than is EI.
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1. Introduction

Organic azides have been recognized for many years as being potentially explosive and experimental work must be carried out with care. Nevertheless, they have many industrial applications as for example seismic explosives [1], semicon- ductors [2], photoresistors [3] and potential as a possible rapid source of gas for airbags. They also are versatile reagents in organic synthesis [4]. Because of their intrinsic instability, their properties are difficult to study and little is known of the mechanisms of their reactions and decompositions. Nevertheless, their thermal decomposition has been studied for many years [5-12] together with their fragmentation in a mass spectrometer initiated by electron impact [13,14]. Some work on their photolysis has also been reported [15]. These tech- niques necessarily involve ill-controlled deposition of energy into the molecule which leads to difficulty in interpretation

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of the mechanisms of decomposition particularly when parallel processes occur and comparisons between azides are attempted. An approach that allows better control over the energy transfer into the azide is to react the azide with Ar^+ in the gas phase. A Fourier transform ion cyclotron resonance mass spectrometer (FTICR) is a convenient platform with which to study these reactions. This allows not only unambiguous identification of the product ions because of the high resolution of the FTICR but also allows the ion concentration-time profiles to be obtained so that a kinetic analysis can be performed. We have investigated the reaction of Ar^+ with three azidonitriles and determined their fragmentation pathways and associated kinetic profiles.

2. Experimental

The synthesis and properties of 3-azidopropionitrile, 2-azidopropionitrile, and acetonitrile have been described elsewhere (F. Martins, M.F. Duarte, M.T. Fernadez, G.J. Langley, P. Rodrigues, M.T. Barros, M.L. Costa, submitted for publication).

The FTICR mass spectrometer used is a Bruker/Spectrospin CMS47X equipped with a 4.7 T magnet and a cylindrical 60 mm × 60 mm 'infinity' cell. A mixture of argon, at a pressure of 9×10^{-8} mbar, and the azide, at a pressure of 9×10^{-9} mbar, was initially ionised by 70 eV electrons. All ions except $^{40}Ar^+$ were ejected from the cell. The Ar^+ was allowed to react with the azidonitrile for various time periods (typically up to 5 s in 0.5 s intervals) and the mass spectrum recorded. All ions with abundances ≥1% of the total ion abundance were selected and their abundances entered into an Excel spreadsheet. The masses of these ions were also recorded to give their unambiguous empirical formulae. The abundances were normalised at each time interval and the files exported into the mathematical package VisSim^{TM} for analysis.

3. Results

For all three azidonitriles it was found that the Ar^+ decayed exponentially. An example is given in Fig. 1. The first order rate coefficients were all in the region of $1.2 \, s^{-1}$; this combined with the nominal pressures of the azidonitriles ($\sim 9 \times 10^{-9}$ mbar) gave second order rate constants $\sim 5 \times 10^{-9}$ molecules^{-1} cm^3 s^{-1}. These are greater than the collisional rate (as the dipole moments and polarizabilities of the azides are unknown, k_{ADO} cannot be calculated) and it is concluded that the initial reactions are proceeding at the collisional rate and that the pressure of the azidonitriles was underestimated by a factor of 2 or so. It should be noted that where rate constants for the reaction of rare gas ions with polar molecules have been determined, they were usually equal to k_{ADO} within experimental error [16]. Inspection of the time profiles of the product ions showed which are primary products and which are secondary products, i.e., formed by further reaction of the primary product ions with the neutral azidonitrile. Analysis of the time profiles allowed the determination of the branching ratios of the products and whether or not they reacted further and if so at what rate. Examples are shown in Figs. 2–4. In some cases it was possible to determine which secondary products arose from which primary products. This was not always feasible due to the paucity and quality of the kinetic data, the multiplicity of product ions, and ambiguities caused by similar rate profiles. The results for each of the
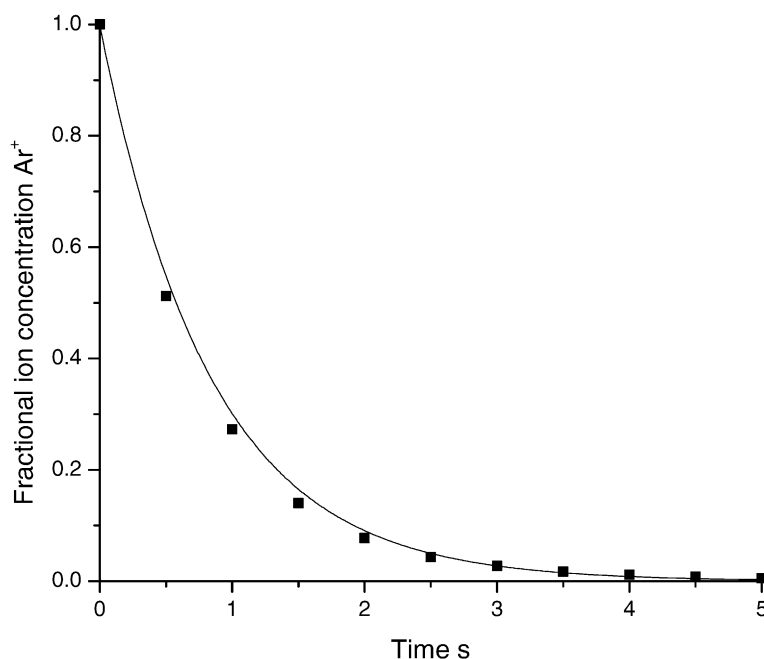

Fig. 1. Time profile of Ar^+ in its reaction with 3-azidopropionitrile, **I**.
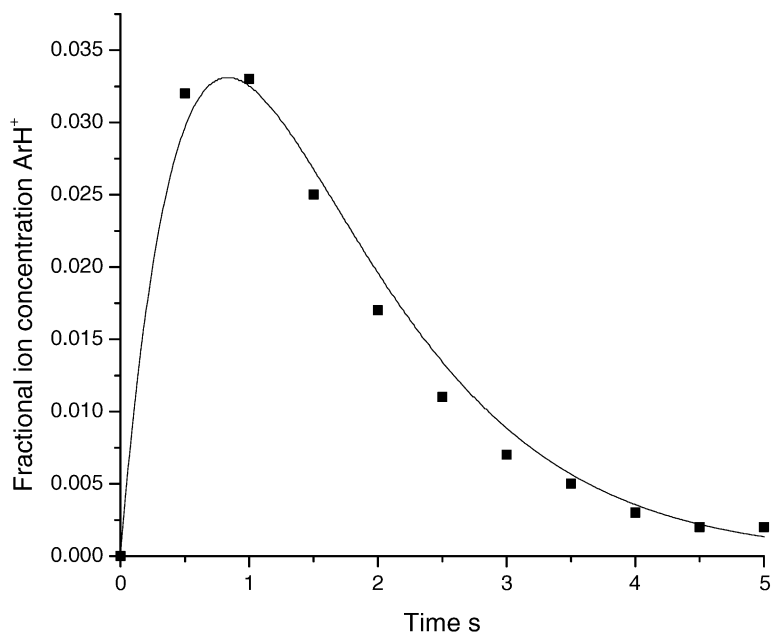
Fig. 2. Time profile for the ArH$^+$ ion in the reaction of Ar$^+$ with 3-azidopropionitrile, **I**.

three azidonitriles will be discussed in turn before an attempt is made to draw the results together.

3.1. 3-Azidopropionitrile—N$_3$CH$_2$CH$_2$CN (**I**)

Ions with abundances $\geq$1% are given in Table 1. These account for $\sim$95% of the ions present.

The primary product ions together with their branching ratios and subsequent rates of further reaction are given in

Table 2. It should be noted that the sum of the branching ratios of the species listed is $\sim$0.8 and this reflects the experimental error in the data. Similarly, the rates of further reaction are subject to error; what is certain however is that the ions in Table 2 are all primary ions, and there are no other ions in any significant amounts that have time profiles which would correspond to their being primary products, and whilst there is uncertainty concerning the absolute values of the rates of their further reaction, the fact that they react further is not in doubt.
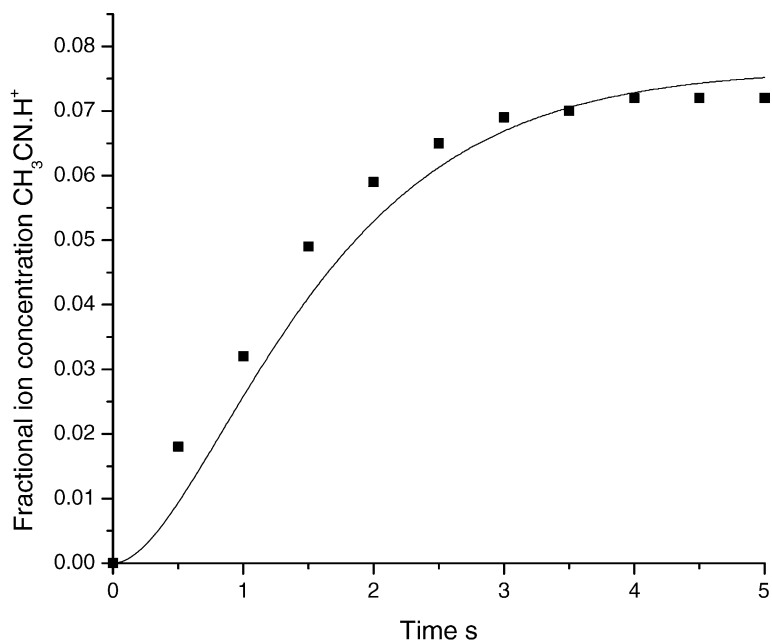

Fig. 3. Time profile for the CH$_3$CN·H$^+$ ion in the reaction of Ar$^+$ with 3-azidopropionitrile, **I**.
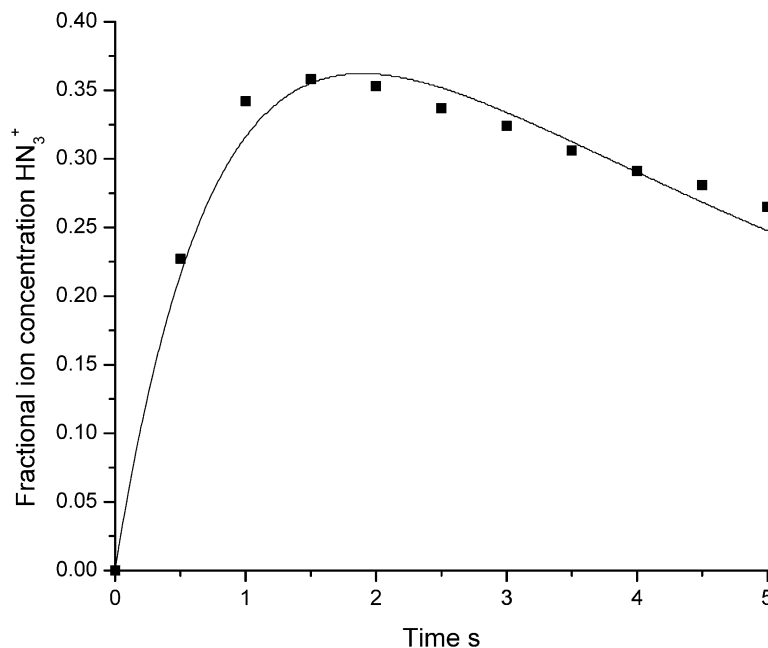
Fig. 4. Time profile for the HN_3^+ ion in the reaction of Ar^+ with 3-azidopropionitrile, **I**.

Table 1
Major ions present in the reaction of Ar^+ with 3-azidopropionitrile, **I**

Measured mass	Empirical formula	Calculated mass
28.01785	CH_2N^+	28.01872
39.96128	Ar^+	39.96162
40.01762	$C_2H_2N^+$	40.01872
40.96913	ArH^+	40.96945
41.02545	$C_2H_3N^+$	41.02655
41.03805	$C_3H_5^+$	41.03913
42.0333	$C_2H_4N^+$	42.03437
43.01727	HN_3^+	43.01704
53.01267	$C_3H_3N^+$	53.02655
54.03307	$C_3H_4N^+$	54.03437
58.04047	$CH_4N_3^+$	58.04051
59.04825	$CH_5N_3^+$	59.04834
60.05157	$CH_6N_3^+$	60.05616
67.02827	$C_3H_3N_2^+$	67.02962
97.04931	$C_3H_5N_4^+$	97.05141

The dominant secondary product ions are $C_2H_4N^+$, $C_3H_4N^+$ (with identical time profiles), $C_3H_5N_4^+$ and $CH_5N_3^+$. The time profiles for $C_2H_4N^+$ and $C_3H_4N^+$ indicate that they are formed by reaction of ArH^+ with 3-azidopropionitrile at, not surprisingly, the collisional rate and neither reacts further. Protonated 3-azidopropionitrile, IH^+, is seen as a secondary product and this too does not react further.

IH^+ will be formed by low energy proton transfer (given the fragility of the azidonitriles a highly exothermic proton transfer is expected to cause fragmentation). Assigning the structure $HCN·H^+$, i.e., protonated hydrogen cyanide to CH_2N^+ makes this a likely precursor to IH^+. The time profiles and branching ratios are not sufficiently well defined for this to be a definite assignment of $HCN·H^+$ as the precursor to IH^+ but it seems likely that it is so, at least in part. Another potential precursor is $CH_4N_3^+$ if this is assigned the structure $CH_3N_3·H^+$, i.e., protonated methyl azide. Combining the two gives good agreement with the time profile for IH^+.

The trace product $CH_6N_3^+$ has the same time profile as the dominant product $CH_5N_3^+$ presumably indicating a common origin. The ion $C_3H_5^+$ is seen in trace amounts. The empirical formulae of these three secondary products suggests that at least some of their presumed precursor primary product ions react with M via electrophilic attack rather than mere charge or proton transfer. None of these trace ions reacts further.

3.2. 2-Azidopropionitrile—$N_3CH(CH_3)CN$ (**II**)

Ions with abundances $\geq 1\%$ are given in Table 3. These account for $\sim 95\%$ of the ions present (Tables 4 and 5).

Only data covering the early part of the reaction were obtained for the 2-azidopropionitrile than were obtained for

Table 2
Primary ions in the reaction of Ar^+ with 3-azidopropionitrile, **I**

Ion	ArH^+	CH_2N^+	$C_2H_2N^+$	$C_2H_3N^+$	HN_3^+	$C_3H_3N^+$	$CH_4N_3^+$
Branching ratio	0.09	0.04	0.06	0.02	0.5	0.06	0.05
k_2 (s^{-1})	1.2	0.35	0.45	0.45	0.17	0.85	0.17

The branching ratios and rates of subsequent reaction are approximate.

Table 3
Major ions present in the reaction of Ar^+ with 2-azidopropionitrile, **II**

Measured mass	Empirical formula	Calculated mass
28.01800	CH_2N^+	28.01872
39.96147	Ar^+	39.96162
41.02588	$C_2H_3N^+$	41.02655
42.03369	$C_2H_4N^+$	42.03437
53.01355	$C_2HN_2^+$	53.01397
54.03377	$C_3H_4N^+$	54.03437
67.02908	$C_3H_3N_2^+$	67.02962
97.05165	$C_3H_5N_4^+$	97.05141

Table 4
Primary ions in the reaction of Ar^+ with 2-azidopropionitrile

Ion	CH_2N^+	$C_2HN_2^+$	$C_3H_3N_2^+$	$C_2H_4N^+$
Branching ratio	0.1	0.6	0.05	0.25
k_2 (s^{-1})	0.4	0.8	0.0	0.0

The branching ratios and rates of subsequent reaction are approximate.

Table 5
Major ions present in the reaction of Ar^+ with 2-azidoacetonitrile, **III**

Measured mass	Empirical formula	Calculated mass
28.01794	CH_2N^+	28.01872
39.96149	Ar^+	39.96162
40.96918	ArH^+	40.96945
53.01303	$C_2HN_2^+$	53.01397
55.02893	$C_2H_3N_2^+$	55.02962
67.02883	$C_3H_3N_2^+$	67.02962
83.03539	$C_2H_3N_4^+$	83.03576

the 3-azidopropionitrile and this precluded a detailed kinetic analysis of the secondary products. The branching ratios for the primary ions did sum to 1.0 and the lack of further reactions of $C_3H_3N_2^+$ and $C_2H_4N^+$ is quite definite. CH_2N^+ and $C_2HN_2^+$ both react further, probably to produce **III**H$^+$ but the lack of data makes this no more than a presumption. Other secondary ions are $C_3H_4N^+$, $C_2H_3N^+$ and a trace of HN_3^+. It is of significance that no appreciable amounts of ArH^+ were observed.

3.3. Azidoacetonitrile—N_3CH_2CN (**III**)

Only three primary ions are observed in the reaction of Ar^+ with azidoacetonitrile. The branching ratios and rates of further reaction are given in Table 6.

The branching ratios for the production of the primary ions total ~0.95. There is only one dominant secondary ion, $C_2H_3N_4^+$ assigned as **III**H$^+$ which is produced from both H_2CN^+ and $C_2HN_2^+$. Trace amounts of $C_2H_3N_2^+$ and

Table 6
Primary ions in the reaction of Ar^+ with azidoacetonitrile

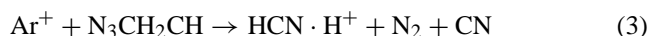| Ion	ArH^+	CH_2N^+	$C_2HN_2^+$
Branching ratio	~0.05	0.3	0.6
k_2 (s^{-1})	~1.2	0.3	1.2

The branching ratio for ArH^+ and its subsequent rate of reaction are approximate.

$C_3H_3N_2^+$ are also observed but in insufficient quantities to allow a kinetic analysis.

4. Structural assignments

Suggested structures for the primary ions and the associated neutral products.

CH_2N^+ is formed from all three azidonitriles and is suggested to be protonated hydrogen cyanide, HCN·H$^+$. The associated neutrals are given in reactions 1, 2, and 3.

$$Ar^+ + N_3CH_2CH_2CN \rightarrow HCN \cdot H^+ + N_2 + C_2H_2N \quad (1)$$

$$Ar^+ + N_3CH(CH_3)CN \rightarrow HCN \cdot H^+ + N_2 + C_2H_2N \quad (2)$$

$$Ar^+ + N_3CH_2CH \rightarrow HCN \cdot H^+ + N_2 + CN \quad (3)$$

C_2H_2N is not listed in the NIST WebBook [17]: a structure such as $CH_2C=N$ similar to a nitrene seems reasonable. Whilst a C_2N radical is known (and could theoretically be formed along with molecular hydrogen), it has the structure CNC and is thus considered to be unlikely as although such a backbone could be formed via a Curtius rearrangement, it has been shown that hydrogen migrates preferentially to carbon [18,19]. That a C_2N radical can be formed from at least **I** is shown in reaction (8).

$C_2H_2N^+$ is only formed from **I** and, whilst no common structure is suggested, it is presumed to have the structure $^+CH_2CN$. The associated neutral products are shown in reaction 4.

$$Ar^+ + N_3CH_2CH_2CN \rightarrow C_2H_2N^+ + H + N_2 + HCN \quad (4)$$

$C_2H_3N^+$ is only seen as a primary ion from **I** although it also appears as a secondary ion from **II**. It is suggested to have the structure of the molecular ion of acetonitrile, CH_3CN^+. The associated neutral products for the formation from are shown in reaction 5.

$$Ar^+ + N_3CH_2CH_2CN \rightarrow CH_2CN^+ + N_2 + HCN \quad (5)$$

As CH_3CN^+ is not a primary ion from **II** but is formed by the reaction of $N_3CH(CH_3)CN^+$ with **II**, no neutral products can be suggested.

HN_3^+ is only seen as a primary product ion from **I** and can only be the molecular ion of hydrogen azide or hydrazoic acid. Although traces are seen with **I** and **III**, it cannot be ascertained whether they are formed in a primary or secondary reaction. The associated neutral is suggested to be 2-propenenitrile or acrylonitrile seen in reaction 6.

$$Ar^+ + N_3CH_2CH_2CN \rightarrow HN_3^+ + CH_2CNCN \quad (6)$$
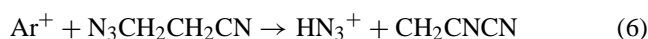
$C_3H_3N^+$ is only seen as a primary product ion from **I** and is suggested to have the structure of the molecular ion of 2-propenenitrile with the associated neutral product being HN as shown in reaction 7.

$$Ar^+ + N_3CH_2CH_2CN \rightarrow CH_2CNCN^+ + NH_3 \quad (7)$$
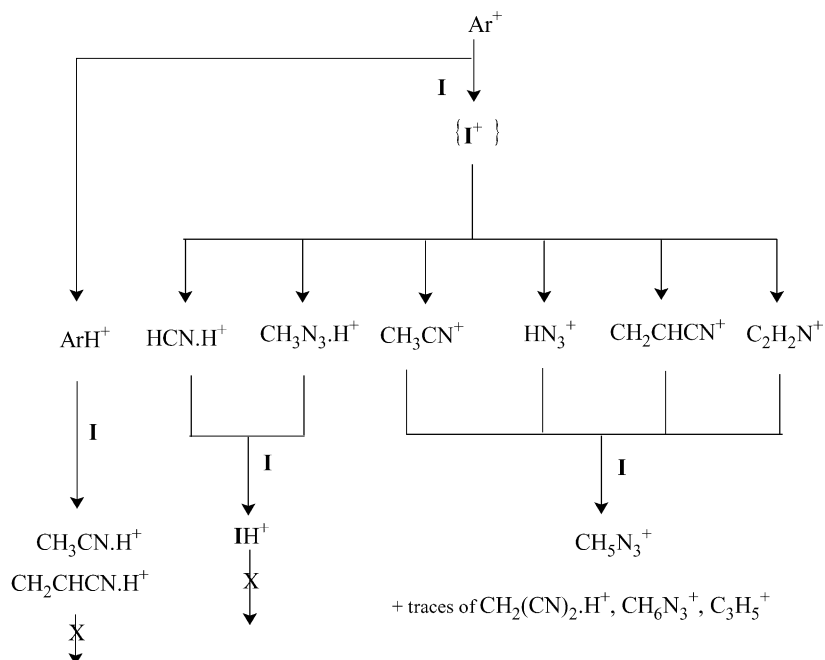
Fig. 5. Reaction pathways for Ar^+ and 3-azidopropionitrile, **I**.

This is the reverse of reaction 6.

$CH_4N_3^+$ is only seen as a primary product ion from **I** and is suggested to have the structure of protonated methyl azide.
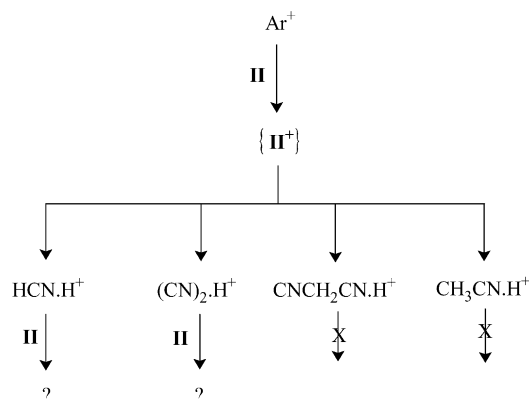
$$Ar^+ + N_3CH_2CH_2CN \rightarrow CH_3N_3 \cdot H^+ + C_2N \quad (8)$$
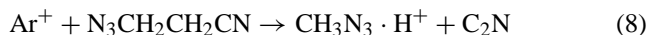
For a discussion on C_2N see Section 2.1 above.

$C_2HN_2^+$ is a primary product from both **I** and **III** and is suggested to be protonated cyanogen, $CNCN \cdot H^+$. The associated neutral products are shown in reactions and 10.

$$Ar^+ + N_3CH(CH_3)CN \rightarrow CHCN \cdot H^+ + N_2 + CH_2NH \quad (9)$$

$$Ar^+ + N_3CH_2CN \rightarrow CHCN \cdot H^+ + H + N_2 \quad (10)$$

The neutral product CH_3N is suggested to be methanimine (methyleneimine) which is listed in the NIST WebBook [17].

$C_2H_4N^+$ is a primary product from **II** and a secondary product from **I** and is suggested to be protonated acetonitrile, $CH_3CN \cdot H^+$. The associated neutral products from **II** are shown in reaction 11.

$$Ar^+ + N_3CH(CH_2)CN \rightarrow CH_3CN \cdot H^+ + N_2 + CN \quad (11)$$

$C_3H_3N_2^+$ is a primary product from **II** and a secondary product from **I** and **III** and is suggested to be protonated malononitrile $CNCH_2CN \cdot H^+$. The associated neutral product from **II** is shown in reaction 12.

$$Ar^+ + N_3CH(CH_3)CN \rightarrow CHCH_2CN \cdot H^+ + H + N_2 \quad (12)$$

Fig. 6. Reaction pathways for Ar^+ and 2-azidopropionitrile, **II**.
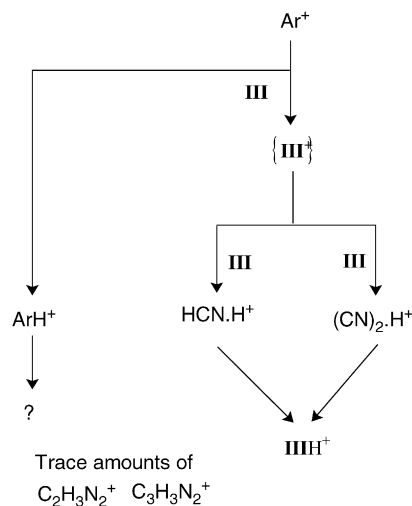
Fig. 7. Reaction pathways for Ar^+ and azidoacetonitrile, **III**.

Suggested structures for some of the secondary ions have been given above. The remaining ions will now be discussed.

$C_3H_4N^+$ is a secondary ion from both **I** and **II** and is suggested to be protonated 2-propenenitrile, $CH_2CHCN\cdot H^+$.

$C_2H_3N_2^+$ is only formed from **III** and is suggested to have the structure of a protonated cyanoimine, $NHCHCN\cdot H^+$.

$CH_5N_3^+$ and $CH_6N_3^+$ are secondary product ions from **I**, the former being the dominant secondary ion by far. No structures are suggested.

$C_3H_5^+$ is a trace secondary ion from **I** and is suggested to be protonated propyne, allene, or cyclopropene.

These results are summarised in Figs. 5–7.

5. Discussion

5.1. The initial reaction

There are two possible mechanisms for the reaction of Ar^+ with the azidonitriles, M. These are hydrogen abstraction to give ArH^+ and charge transfer to give the molecular ion M^+. ArH^+ is produced in significant, albeit small, amounts only from **I** and **III**. We presume that it is not formed from **II** as the hydrogen adjacent to the nitrile and azide groups would prefer to be abstracted as a hydride ion leaving a stable carbocation and the methyl hydrogens are too unreactive to compete with charge transfer.

The molecular ion M^+ is not observed but this is not surprising as it will be formed with an excess internal energy of several electron volts, the difference between the ionisation energy of Ar (15.8 eV) and that of the azidonitrile (probably in the region of 8–10 eV). It can therefore be expected to have only a transient existence and to immediately fragment. Unfortunately the lack of thermodynamic data on the azidonitriles precludes a detailed thermodynamic analysis of the fragmentation pathways, not only for these primary fragmentations but also the secondary ones. The reaction enthalpies can be calculated for some of the reactions using data from the NIST webbook [17]:

Reaction (3) $\Delta H = -135\,\text{kJ mol}^{-1} - \Delta H_f\text{III}$

Reaction (5) $\Delta H = -212\,\text{kJ mol}^{-1} - \Delta H_f\text{I}$
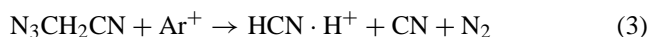
Reaction (6) $\Delta H = -355\,\text{kJ mol}^{-1} - \Delta H_f\text{I}$

Reaction (9) $\Delta H = -289\,\text{kJ mol}^{-1} - \Delta H_f\text{II}$

Reaction (10) $\Delta H = -140\,\text{kJ mol}^{-1} - \Delta H_f\text{III}$

Reaction (11) $\Delta H = -271\,\text{kJ mol}^{-1} - \Delta H_f\text{II}$

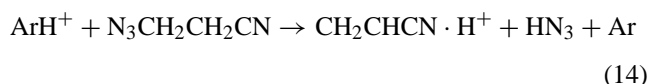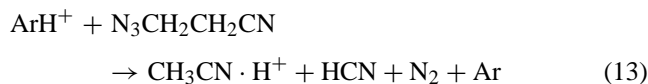Reaction (12) $\Delta H = -231\,\text{kJ mol}^{-1} - \Delta H_f\text{II}$

In three instances, one for each of the azidonitriles (see reactions 8, 11 and 3) all of the hydrogen atoms in the parent neutral are retained in the product ion

$$N_3CH_2CH_2CN + Ar^+ \rightarrow CH_3N_3\cdot H^+ + C_2N \qquad (8)$$

$$N_3CH(CH_3)CN + Ar^+ \rightarrow CH_3CN\cdot H^+ + CN + N_2 \qquad (11)$$

$$N_3CH_2CN + Ar^+ \rightarrow HCN\cdot H^+ + CN + N_2 \qquad (3)$$

which suggests some unusual hydrogen migrations. Of particular interest is reaction (3) where either of the nitrogens attached to carbon could be retained in the ionic product. A study of a isotopomer of **III** with the cyano group labeled with ^{13}C would be informative.

5.2. Secondary (and tertiary) reactions

ArH^+ reacts with **I** to give two ionic products as shown in reactions 13 and 14.

$$\begin{aligned}ArH^+ &+ N_3CH_2CH_2CN \\ &\rightarrow CH_3CN\cdot H^+ + HCN + N_2 + Ar \qquad (13)\end{aligned}$$

$$ArH^+ + N_3CH_2CH_2CN \rightarrow CH_2CHCN\cdot H^+ + HN_3 + Ar \qquad (14)$$

The neutral products are consistent with the pathway followed being determined by the position of protonation, i.e., protonation on the nitrile moiety leading to reaction 13 and protonation on the azide leading to reaction 14. Such selective fragmentation may also reflect the lower ΔH_f of ArH^+ (1161 kJ mol^{-1}) compared with that of Ar^+ (15.8 eV, 1522 kJ mol^{-1}). It is unfortunate that we do not have data for **II** and **III**.

The behaviours of the remaining proton sources, $HCN\cdot H^+$, $CH_3N_3\cdot H^+$, $(CN)_2\cdot H^+$, $CNCH_2CN\cdot H^+$, $CH_3CN\cdot H^+$, and $CH_2CHCN\cdot H^+$ are interesting. $HCN\cdot H^+$ transfers a proton to the azidonitriles **I** and **III** to give stable $\textbf{I}H^+$ and $\textbf{III}H^+$, respectively and reacts similarly with **II** presumably to give $\textbf{II}H^+$. $(CN)_2\cdot H^+$ formed as a primary ion from **II** and a secondary ion from **III** reacts similarly. None of the ions $CNCH_2CN\cdot H^+$, $CH_3CN\cdot H^+$, and $CH_2CHCN\cdot H^+$ transfers a proton to any of the azidonitriles. The proton affinities of the various species are shown in Table 7 along with their heats of formation [18].

Proton transfer, if it occurs, will be effectively irreversible under the conditions obtaining in the FTICR cell. It is unlikely to have an energy barrier on the reaction coordinate and thus if exoergic will occur at the collisional rate. This is exemplified by the reaction of ArH^+ with **I** and **III** (it is irrelevant that the exoergodicity of the proton transfer is sufficient to cause fragmentation). Proton transfer to **III** from

Table 7
Proton affinities and heats of formation

M	Proton affinity (kJ mol^{-1})	ΔH_f (M) (kJ mol^{-1})	ΔH_f (MH$^+$) (kJ mol^{-1})
Ar	369	0	1161
$(CN)_2$	675	309	1164
HCN	713	135	952
$CNCH_2CN$	723	266	1073
CH_3CN	779	74	816
CH_2CHCN	785	184	929

$(CN)_2 \cdot H^+$ also occurs at the collisional rate but that from $HCN \cdot H^+$ occurs significantly below the collisional rate. This suggests that proton transfer from $HCN \cdot H^+$ to **III** is thermoneutral or slightly endoergic, i.e., the PA of **III** is just below that of HCN but equal to or above that of $(CN)_2$. Proton transfer to **II** from both $HCN \cdot H^+$ and $(CN)_2 \cdot H^+$ is significantly below the collisional rate with that from $HCN \cdot H^+$ being the slowest. This suggests that the PA of **II** is slightly below those of both HCN and $(CN)_2$. Finally, proton transfer to **I** from $HCN \cdot H^+$ is also below the collisional rate indicating again that the PA of the azidonitrile, in this case **I**, is slightly below that of HCN. The suggested proton transfer from $CH_3N_3 \cdot H^+$ is also significantly below the collisional rate suggesting that the PA of CH_3N_3 is in the region of $700 \, kJ \, mol^{-1}$. This estimation is only approximate as the values of PAs in Table 7 were obtained under thermal conditions unlike those obtaining in the present study. Nevertheless, this analysis is consistent with the observation that proton transfer from ArH^+ is sufficiently exoergic to initiate fragmentation of the azidonitrile but that from $HCN \cdot H^+$ and $(CN)_2 \cdot H^+$ leads only to the stable protonated azidonitrile.

5.3. Comparison with previous studies

Unfortunately the thermal decomposition of the azidonitriles considered in the present work has not been reported. Their fragmentation following electron impact ionisation (EI) in a tandem mass spectrometer has been investigated (F. Martins, M.F. Duarte, M.T. Fernadez, G.J. Langley, P. Rodrigues, M.T. Barros, M.L. Costa, submitted for publication) and a comparison of fragmentation patterns is merited. In the EI study it was found that the ion with *m/z* 28 did not arise from decomposition of the molecular ions and it was suggested that it arose from the ionisation of thermal decomposition products formed in the inlet system. This is not the case in the present system in which the azidonitrile is at ambient temperature during the course of the experiment. However, in the previous EI study (data not shown), the high resolution mass measurements proved the existence of more than one ion with nominal *m/z* 28, N_2^+ being the most abundant followed by CH_2N^+. Therefore, $HCN \cdot H^+$ seems to be the only common ion that occurs in all three compounds in both studies.

For 3-azidopropionitrile the primary ions in the EI study are $CH_2N_3^+$, $C_3H_4N_2^+$, $C_3H_3N_2^+$, and $C_2H_3N^+$. The first two are not observed at all in the present work, the third is only observed in trace amounts as a secondary product ion. Another major difference is that the ion $C_2H_2N^+$ is a secondary product ion in the EI study as shown by linked scans whereas it is a primary product ion in the present study.

For 2-azidopropionitrile the EI study shows four primary product ions, $C_3H_4N_2^+$, $C_3H_3N_2^+$, $C_3H_4N_2^+$, and $C_2H_3N^+$. In the present study the first is not observed, the second is but is stable whereas it fragments in the EI study, the third is not observed and the fourth is a secondary product ion. $C_2HN_2^+$ is a dominant ion in both systems but in the EI study it is a secondary product ion whereas it is the dominant primary ion in the present study. Finally, $C_2H_2N^+$ is a dominant secondary ion in the EI study but not observed in the present study.

For azidoacetonitrile the EI study shows only two dominant primary ions $C_2HN_2^+$ and $C_2H_2N_2^+$. The first is also a dominant ion in the present study whereas the second is not seen at all.

The lack of correlation in the fragmentation pathways resulting from the two ionisation techniques is, at first sight, somewhat surprising. In the present system sufficient energy is transferred from the Ar^+ to the azidonitriles that the molecular ion immediately fragments and is not detected. Relatively few primary fragmentation products are observed however, six from 3-azidopropionitrile, four from 2-azidopropionitrile, and two from azidoacetonitrile. In the EI system, applying the same criterion of only analysing peaks with intensities $\geq 1\%$, in addition to strong molecular ion peaks, eleven peaks were observed from 3-azidopropionitrile, ten from 2-azidopropionitrile, and six from azidoacetonitrile. The number of peaks in the EI system include that at *m/z* 28 which is attributed to a thermal decomposition product, but, even excluding this, considerably more fragmentation occurs in the EI system. It is interesting that the molecular ions are also observed but whether this is due to a wide range of energy depositions occurs on EI in contrast to the narrow, if not monotonic, range deposited in the present system or the different time scales of the experiments (μs for the EI experiments (F. Martins, M.F. Duarte, M.T. Fernadez, G.J. Langley, P. Rodrigues, M.T. Barros, M.L. Costa, submitted for publication) in contrast with at least ms in the present work) is open to speculation. This supports the suggestion expressed in the Introduction that chemical ionisation with a reagent gas such as argon is a more appropriate technique for investigating the decomposition of such fragile compounds as organic azides.

6. Conclusions

The results presented here have demonstrated that the reaction of Ar^+ with the azidonitriles gives selective fragmentation. Although some common ions are produced, the fragmentation is very dependent upon the structure of the azide. To exploit this approach a much wider range of azides should be investigated together with their isotopomers where possible. The value of using isotopomers to investigate in detail the fragmentation of ions is exemplified by a recent paper on the fragmentation of an organophosphate ion in an ion trap mass spectrometer where three isotopomers were investigated [20]. It is suggested that Ar^+ chemical ionisation is

potentially more appropriate for investigating the decomposition of fragile molecules such as the azidonitriles than is electron impact.

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