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The reaction of the acrylonitrile ion $CH_2{=}CH{-}C{\equiv}N^{\cdot+}$ with HCN: Proton-transport catalysis vs formation of ionized pyrimidine

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ABSTRACT

The CBS-QB3 model chemistry predicts that the title ion–molecule reaction, of potential interest in astrochemistry, yields a stable head-to-tail dimer, $[HC{=}N{-}CH_2C(H)C{\equiv}N]^{\cdot+}$ (**D**1). Cyclization of **D**1 into ionized pyrimidine seems possible, but the initiating 1,2-H shift is close in energy to back-dissociation into $CH_2{=}C(H)CN^{\cdot+}$ (**AN**) + HCN. Less energy demanding is formation of the H-bridged isomers $[CH_2{=}C(CN)H{--}N{\equiv}CH]^{\cdot+}$ and $[HC{\equiv}N{--}HC(H){=}C(H)CN]^{\cdot+}$, whose HCN component may catalyze isomerization of **AN** into $CH_2{=}C{=}C{=}NH^{\cdot+}$ (**AN**1) and $CH{=}C(H)C{=}NH^{\cdot+}$ (**AN**2) respectively. Tandem mass spectrometry based experiments using $^{15}N/^{13}C$ labelling show that cyclization of **D**1 does not occur and that **AN**1 is the predominant reaction product instead.

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1. Introduction

Ion–molecule interactions in the rarefied gas-phase have proven to be a good way to rationalize various reactions of relevance to astrochemistry that are not possible between neutral molecules [1,2]. Such interactions can lead to (de-)protonation [3], isomerization by proton-transport catalysis (PTC) [4–7], and the formation of new product molecules via covalently bonded reaction intermediates.

A case in point is our previous study on the reaction of the acrylonitrile ion $CH_2{=}CHC{\equiv}N^{\cdot+}$ (**AN**) with its neutral counterpart [8], a confirmed species in interstellar dust clouds [2]. The resulting dimer ion dissociates by proton transfer, but it can also rearrange to yield the pyrimidine ion (**PY**) by loss of C_2H_2. Selected Ion Flow Tube (SIFT) experiments by Petrie et al. [9] and Milligan et al. [10] indicate that the dimer formation takes place at close to the collision rate, which implies that its dissociation into **PY** could be relevant to astrochemistry. The prebiotic pyrimidine molecule could also be formed from neutral acrylonitrile and HCN but so far there is no experimental or computational support for this suggestion [11].

An *a priori* more attractive possibility for the gas-phase synthesis of (ionized) pyrimidine involves the reaction of the acrylonitrile *ion* (**AN**) with HCN. This reaction has also been studied in Ref. [9], which reports that it results mainly in adduct formation with varying degrees of H loss. The reaction is evidently exothermic in view of the number of product channels, yet it occurs at only 6% of the collision rate. The authors argue that such a behaviour indicates that the adduct $C_4H_4N_2^{\cdot+}$ does not correspond to a deep well in the **AN**/HCN potential energy surface, a deduction which would remove the pyrimidine ion and its cyclic isomers from contention as possible product ions.

The contention that **AN**/HCN adduct ions would not occupy a deep potential well, whereas the **AN**/$CH_2{=}CHC{\equiv}N$ complexes studied in Ref. [8] do, prompted us to use computational chemistry and complementary experiments to probe the dissociation chemistry of **AN**/HCN complexes generated by the ion–molecule reaction of $CH_2{=}CHC{\equiv}N^{\cdot+}$ with HCN.

The gas-phase synthesis of the pyrimidine ion from **AN** and HCN explored in this study is the analogue of the mechanism proposed in Ref. [8] for the reaction of **AN** with its neutral counterpart. As depicted by Reaction 1 of Scheme 1, **AN** forms a covalently bound head-to-tail dimer with HCN and then proceeds to ring closure and a 1,2-H shift to form the pyrimidine ion.

We have also examined potentially competing reactions, *viz.* the HCN catalyzed isomerization of **AN** and protonation of HCN by **AN**, shown as Reactions 2 and 3 of Scheme 1.

All three reactions appear to be energetically possible but RRKM-based reaction-rate constant calculations [12] indicate that Reaction 1 cannot effectively compete with the HCN catalyzed isomerization(s) of Reaction 2. Indeed, our experiments with the isotopically labelled compounds $H^{13}CN$ and AN(^{15}N) indicate that the adduct ions do not cyclize into the pyrimidine ion. Instead, it will be shown that HCN catalyzes the transformation of $CH_2{=}CHC{\equiv}N^{\cdot+}$(**AN**) into $CH_2{=}C{=}C{=}NH^{\cdot+}$ (**AN**1).

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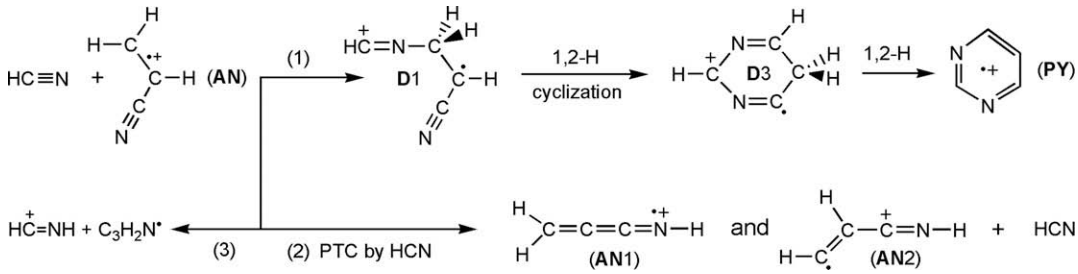


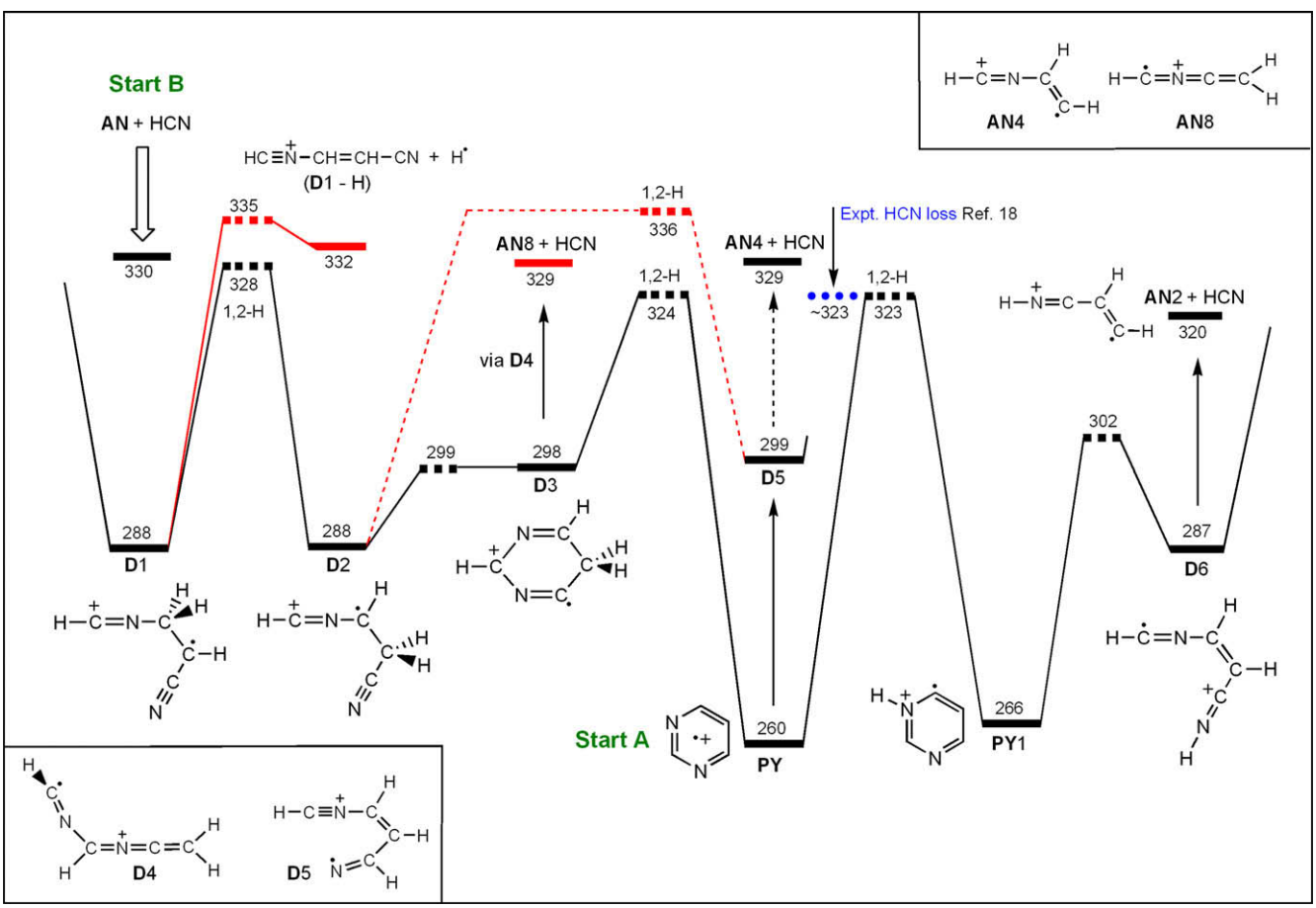
Scheme 1.

2. Theoretical and experimental methods

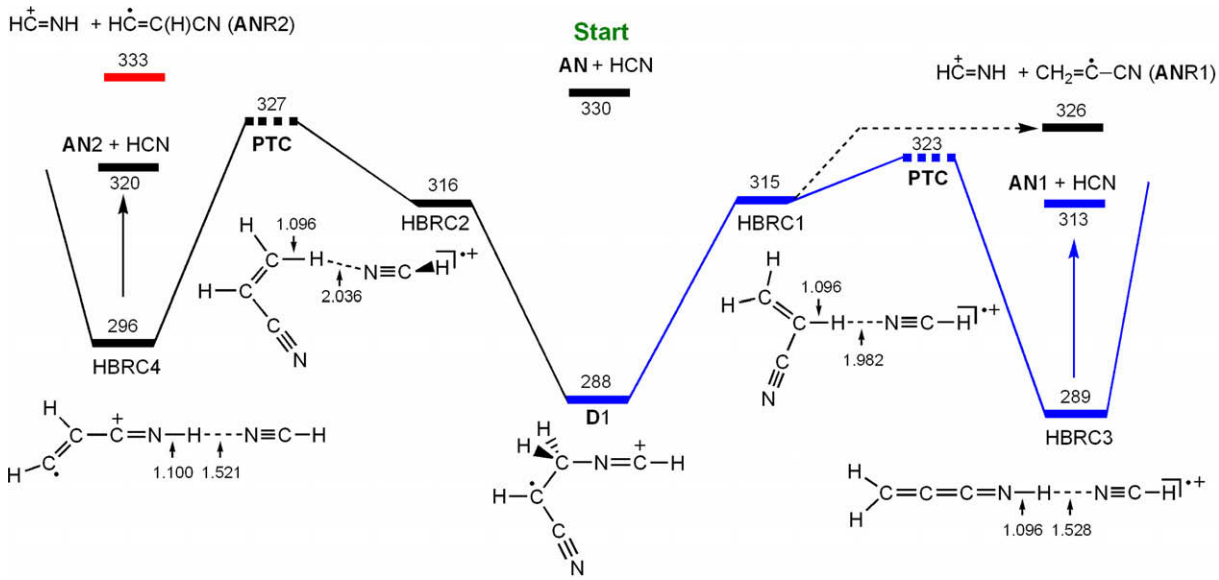
The calculations were performed with the CBS-QB3 model chemistry [13] using the Gaussian 98 and 03 suite of programs [14]. For selected transition state searches Gamess-UK [15] was used. Enthalpies of formation ($\Delta_f H^0_{298}$ values in kcal mol^{-1}) and energies for the various ions depicted in the energy level diagrams of Schemes 2 and 3 are presented in Table 1. The CBS-QB3 derived $\Delta_f H^0_{298}$ values for the $C_3H_3N^{\cdot+}$ isomers $CH_2{=}C(H)CN^{\cdot+}$ (**AN**), $CH_2{=}C{=}C{=}NH^{\cdot+}$ (**AN1**), $HC{=}C(H)C{=}NH^{\cdot+}$ (**AN2**), $HC{=}C(H)N{=}CH^{\cdot+}$ (**AN4**) and $CH_2{=}C{=}N{=}CH^{\cdot+}$ (**AN8**), 298, 281, 288, 299 and 297 kcal mol^{-1} respectively, were taken from Ref. [20]. Those for the radicals $CH_2{=}C^{\cdot}{-}CN$ (**AN**R_1) and $HC^{\cdot}{=}C(H)CN$ (**AN**R_2),100 and 108 kcal mol^{-1} respectively, are from Ref. [8]. The CBS-QB3 298 K values for $H^{\cdot}$, HCN and $HCNH^+$ are 52, 32 and 226 kcal mol^{-1} respectively.

The correctness of transition states was verified (where not trivially evident) by means of Intrinsic Reaction Coordinate (IRC) calculations. Several of the calculations showed spin contamination beyond the accepted values (0.75–0.79). The largest $\langle S^2 \rangle$ value (1.50) was found for TS **D5** → **PY**. It is not expected (see Ref. [8]) that this will greatly affect the estimated (±2 kcal mol^{-1}) accuracy of the calculated enthalpies of the minima presented in Table 1. For example, a CBS-APNO calculation [16] on TS **D5** → **PY** yields 299 kcal mol^{-1}, almost equal to the CBS-QB3 result. The complete set of results including the optimized geometries (which are also found in Ref. [12]) is available from the authors upon request.

The exploratory experiments were performed with the McMaster VG Analytical ZAB-R mass spectrometer of BEE geometry (B = magnet, E = electric sector) equipped with a standard chemical ionization source operating at 120 °C, as described in more detail in Ref. [8]. The repeller voltage was held close to 0 V and the primary



Scheme 2. The mechanistic proposal for the formation of ionized pyrimidine in the ion–molecule reaction of HCN and ionized acrylonitrile (**AN**). The numbers refer to CBS-QB3 derived 298 K enthalpies in kcal mol^{-1}.



Scheme 3. Proton-transport catalysis (PTC) of the acrylonitrile ion (**AN**) with HCN as the catalyst. The numbers refer to CBS-QB3 derived 298 K enthalpies in kcal mol^{-1}.

Table 1
CBS-QB3 derived enthalpies of formation (kcal mol^{-1}) and total energies (Hartree) of stable ions and transition states involved in the ion–molecule chemistry of ionized acrylonitrile and HCN.

Ion	Structure	CBS-QB3 E (total) [0 K]	QB3 $\Delta_f H^0_{298}$	Transition State	CBS-QB3 E (total) [0 K]	QB3 $\Delta_f H^0_{298}$
D1	Scheme 1/2	−263.49108	288	TS **D**1 → H loss	−263.41648	335
D1-H	Scheme 2 (H loss)	−262.92228	280	TS **D**1 → 2	−263.42636	328
D2	Scheme 2	−263.48996	288	TS **D**2 → 3	−263.47093	299
D3	Scheme 1/2	−263.47297	298	TS **D**2 → 5	−263.41275	336
D4	Scheme 2	−263.46756	303	TS **D**3 → 4	−263.45368	311
D5	Scheme 2	−263.47266	299	TS **D**3 → **PY**	−263.43094	324
D6	Scheme 2	−263.49249	287	TS **D**5 → **PY**	−263.46953	300
PY	Scheme 1/2	−263.53204	260	TS **PY** → **PY**1	−263.43340	323
PY1	Scheme 2	−263.52314	266	TS **PY**1 → **D**6	−263.46678	302
HBRC1	Scheme 3	−263.44906	315			
HBRC2	Scheme 3	−263.44810	316	TS **HBRC**1 → D1	−263.44788	315
HBRC3	Scheme 3	−263.49064	289	TS **HBRC**1 → 3	−263.43521	323
HBRC4	Scheme 3	−263.47936	296	TS **HBRC**2 → 4	−263.42936	327

electron ionization (EI) was accomplished with 100 eV electrons. Gaseous acrylonitrile, HCN and CO_2 in a c. 1:3:10 molar ratio were admitted to the ion source via separate inlet systems at a total indicated pressure (monitored by a remote ionization gauge) of 7–10 × 10^{-5} Torr. Metastable ion (MI) and collision-induced dissociation (CID) mass spectra [17] using O_2 as the collision gas were obtained in the second field-free-region (2ffr).

The ion–molecule reaction of *mass-selected* acrylonitrile ions (generated by EI) with HCN was performed on the Mons AutoSpec 6F, a six-sector magnetic deflection instrument. The instrument is equipped with three cells (C_{1-3}) to realize high-energy collision-induced dissociations and an rf-only hexapole (HEX) reaction chamber for studies of associative ion–molecule reactions [7] so that the configuration is: $C_1E_1B_1C_2E_2$-HEX-$E_3B_2C_3E_4$.

In brief, the experiment involves mass selection of a beam of *m/z* 53 acrylonitrile ions (8 keV) using the first three sectors. Next, the ions are decelerated to ~5 eV in front of the hexapole cell to optimize the yield of the associative ion–molecule reactions with gaseous HCN – at a pressure of ~5 × 10^{-4} mbar, as measured with a Pirani gauge located inside the cell. Following reacceleration to 8 keV, ions leaving the hexapole cell are mass analyzed by scanning the field of B_2. Finally, the mass-selected *m/z* 80 or *m/z* 53 ions are subjected to CID with O_2 in chamber C_3, and their spectra, see Fig. 2d and 1c/d, are obtained by scanning sector E_4.

Acrylonitrile, Acrylonitrile-^{15}N (ICON, New Jersey, USA) and CO_2 were of research grade and used without further purification. $H^{13}CN$ was synthesized from $K^{13}CN$ (BOC, London, UK).

3. Results and discussion

3.1. Formation of the pyrimidine ion from the ion–molecule reaction *AN + HCN*

In our discussion of pyrimidine ion (**PY**) formation from **AN** + HCN, the potential energy diagram of Scheme 2 will serve as a guide. The right-hand side of the Scheme (START A), which describes the dissociation of **PY** by loss of HCN, will be examined first because it has been studied in considerable detail [18,19].

The PEPICO study of Ref. [18] shows that **PY** → $C_3H_3N^{\cdot+}$ + HCN is the reaction of lowest energy requirement with a threshold at ~323 kcal mol^{-1}. A subsequent detailed study [19] of **PY** and several of its 1,2-H shift isomers including **PY**1 of Scheme 2, concludes that the $C_3H_3N^{\cdot+}$ product ion is not **AN**, but perhaps the keteneimine isomer $CH_2{=}C{=}C{=}NH^{\cdot+}$ (**AN**1). This conclusion was based on a comparative analysis of the high-energy CID mass spectra of the $C_3H_3N^{\cdot+}$ ions generated from **PY** and **PY**1 with that of **AN**. Indeed, the spectrum of **AN**, see Fig. 1c, is clearly different from the similar but not identical spectra of **PY** and **PY**1, see Fig. 1a/b. Our

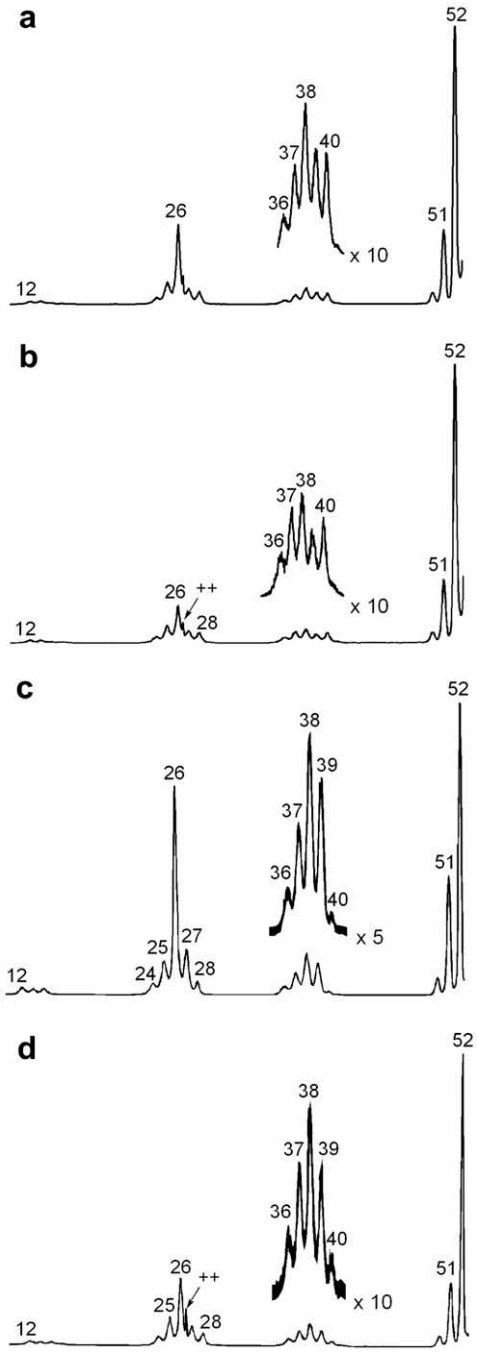


Fig. 1. CID mass spectra of the C_3H_3N ions generated from: (a) low-energy (metastable) pyrimidine (**PY**); (b) pyrimidine-4-ylid (**PY**1) ions; (c) ionized acrylonitrile (**AN**) and (d) the ion–molecule reaction **AN** + HCN.

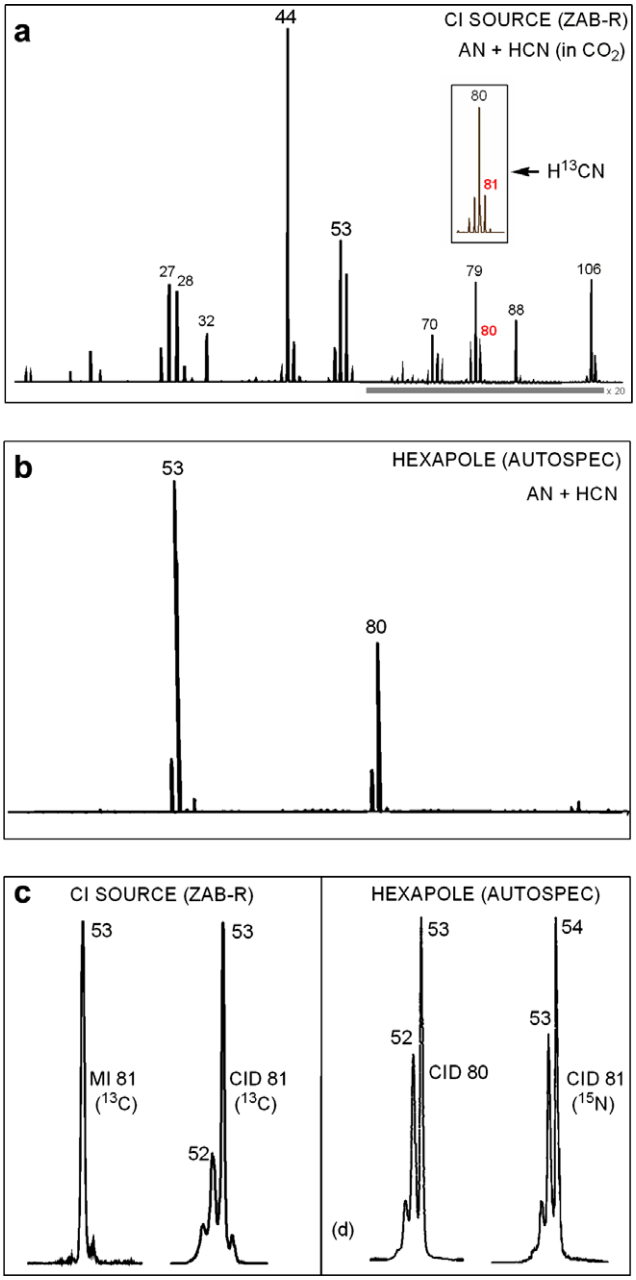


Fig. 2. (a) Chemical ionization mass spectrum of a mixture of $CH_2{=}C(H)CN$, HCN and CO_2; (b) mass spectrum of the products of the ion–molecule reaction **AN** + HCN performed in the hexapole reaction chamber of the Autospec; (c) MI and partial CID spectra of *m/z* 81 adduct ions **AN**/$H^{13}CN$; (d) partial CID spectra of adduct ions **AN**/HCN and **AN**(^{15}N)/HCN.

recent theoretical and experimental study of **AN** and its principal isomers **AN**1–**AN**8 [20] sheds more light on the structure assignment of the spectra of Fig. 1a and b. The spectrum of Fig. 1b appears to be superimposable upon that of the reference spectrum [20] of $HC{=}C(H){-}C{=}NH^{\cdot+}$ (**AN**2), while that of Fig. 1a appears to be compatible with the formation of **AN**2 in admixture with $HC{=}C(H){-}N{=}CH^{\cdot+}$ (**AN**4). The reference spectrum of **AN**4 [20] is close to that of **AN**2 but its *m/z* 26 peak is more pronounced, in line with the energetically more favourable loss of HCN vis-à-vis that of HNC from **AN**2.

The study of Ref. [20] also discusses **AN**1, which is separated from its isomers by prohibitive barriers and represents the global minimum on the $C_3H_3N^{\cdot+}$ PES. Upon CID, **AN**1 is expected to dissociate primarily by loss of H$^{\cdot}$, like its distonic isomer **AN**2. A reference spectrum of pure ions **AN**1 is not available, but the *m/z* 40 peak for loss of CH in the structure diagnostic cluster of ions at *m/z* 36–40 is expected to be insignificant in the spectrum of **AN**1 [20]. This expectation is supported by the CID spectra (not shown) of the collision induced loss of H$^{\cdot}$ from $CH_2{=}C(H)C{=}NH^+$ and loss of D$^{\cdot}$ from $CH_2{=}C(D)C{=}ND^+$.

The proposed formation of **AN**2 and **AN**4 from **PY** is corroborated by the computations of Scheme 2. Dissociation into **AN**2 + HCN occurs via a three-step reaction, whose energy requirement equals the threshold of Ref. [18]. The first step involves a 1,2-H shift in **PY**, whose TS lies at 323 kcal mol^{-1}, to generate **PY**1. A

relatively facile ring opening thereof leads to ion **D**6, which can then dissociate into **AN**2 + HCN. Scheme 2 shows that the proposed co-generation of **AN**4 from low-energy (metastable) ions **PY** is also feasible: the ring-opening **PY** → **D**5 has a relatively low energy requirement and the subsequent direct bond cleavage **D**5 → **AN**4 + HCN is a mere 6 kcal mol^{-1} higher in energy than the **AN**2 formation. That metastable ions **PY**1 generate **AN**2 as the sole $C_3H_3N^{\cdot+}$ reaction product is because the isomerization **PY**1 → **PY** is more energy demanding than the direct dissociation **PY**1 → **D**6 → **AN**2 + HCN. This scenario is consistent with the observation of Ref. [19] that the kinetic energy release [17] associated with the HCN loss from **PY**1 is lower than that from **PY** (13 vs 32 meV). Finally we note that it is unlikely that the circuitous dissociation route **PY** → **D**3 → **D**4 → $CH_2{=}C{=}N{=}CH^{\cdot+}$ (**AN**8) can compete with the direct bond cleavage **PY** → **D**5 → **AN**4.

We now turn to the computational analysis of the formation of **PY** from **AN** + HCN as depicted in Scheme 2 (START B). Theory predicts that the associative ion–molecule reaction leads to the stable covalently bound adduct ion **D**1, whose high stabilization energy is on par with that of the **AN** dimer [8]. **D**1 can isomerize into ion **D**2, via a 1,2-H shift that lies just below the combined enthalpies of **AN** + HCN, but the subsequent 1,2-H shift that would yield the ring-opened pyrimidine ion **D**5 is associated with a prohibitively high barrier. Instead, ions **D**2 may undergo a facile ring closure to form ion **D**3, in which a 1,2 H shift at 324 kcal mol^{-1} completes the transformation of **D**2 into **PY**. Thus the theory of Scheme 2 suggests that the gas-phase synthesis of **PY** via the route **D**1 → **D**2 → **D**3 → **PY** is energetically possible because the energy requirements of the direct bond cleavage dissociations available to **D**1, back-dissociation into **AN** + HCN and loss of H$^{\cdot}$ as depicted in Scheme 2, are slightly higher. Also, loss of HCN from **D**3 may not favourably compete with the transformation **D**3 → **PY**.

This prompted us to perform chemical ionization experiments with a mixture of $CH_2{=}C(H)CN$ and HCN using CO_2 as the bath gas. Fig. 2a shows a typical CI mass spectrum, which displays a great many peaks, including acrylonitrile dimer ions at *m/z* 106 and, less prominently, the desired acrylonitrile/HCN ions at *m/z* 80. The MI mass spectrum of the *m/z* 80 ions only shows a peak at *m/z* 53, which also dominates the CID spectrum. Thus, loss of HCN is the prevailing dissociation but, see Scheme 2, this only allows us to differentiate between **D**1 and **PY** (or a mixture thereof) if the structure(s) of the resulting *m/z* 53 ions can be established by a double collision experiment. Unfortunately, insufficient signal intensity prevented this analysis. Instead, we replaced the HCN of the above CI experiment by $H^{13}CN$, considering that the resulting *m/z* 81 ions, see inset of Fig. 2a, should display loss of both HCN (via **D**5) and $H^{13}CN$ (via **D**6) in their MI and CID spectra if the **D**1($H^{13}CN$) ions have undergone cyclization into **PY**. This appears not to be the case, as witnessed by the spectra of Fig. 2c. These spectra display a specific loss of $H^{13}CN$, indicating that the cyclization does *not* occur.

Given the complexity of the ion–molecule chemistry of the above CI experiment, which is further aggravated by the CO_2 catalyzed isomerization [21] of ionized HCN into $HNC^{\cdot+}$, we have also performed experiments of *mass-selected* **AN** ions with HCN in a hexapole reaction chamber, as described in the Experimental. Fig. 2b shows that in this set-up, the reaction of **AN** and HCN yields *m/z* 80 ions almost exclusively: the minor peaks at *m/z* 52 and 79 result from the collision induced H$^{\cdot}$ loss from *m/z* 53 and the subsequent ion–molecule reaction $C_3H_2N^+$ (*m/z* 52) + HCN → $C_4H_3N_2^+$ (*m/z* 79).

Definitive evidence that the reaction of ionized acrylonitrile with HCN does not yield ionized pyrimidine is provided by a specific ^{15}N labelling experiment. Fig. 2d shows the partial CID spectrum of the *m/z* 80 ions vis-à-vis that of the *m/z* 81 ions obtained by replacing the acrylonitrile with its ^{15}N-labelled analogue. It is seen that the labelled dimer ion specifically loses $HC^{14}N$ and this shows that pyrimidine ions are not formed. In the next Section it will be shown that the reaction leads to the isomerization of **AN** into **AN**1 instead.

3.2. Protonation and proton-transport catalysis in the AN/HCN dimer ions

As indicated in Scheme 3, energy-rich dimer ions **D**1 can readily adopt the configuration of the hydrogen-bridged radical cations [22] **HBRC**1 and **HBRC**2. Proton transfer in **HBRC**1 yields $HC{=}NH^+$ + **AN**R1, whose energy level lies below that of **AN** + HCN. **HBRC**2 would yield $HC{=}NH^+$ + **AN**R2, but this process is too energy demanding to compete with the back-dissociation of the dimer ion **D**1.

The MI spectrum of the dimer ion **D**1 displays no *m/z* 28 peak for $HC{=}NH^+$, and its intensity is only marginal in the CID spectrum (not shown). This raises the question whether the incipient $HC{=}NH^+$ ions in the HBRC's can donate a proton back to the incipient radical to generate an **AN** isomer of lower enthalpy.

The proton-transport catalysis criterion [3–6] predicts HCN to be an efficient catalyst for the isomerization of **AN** in the ion–molecule encounter complex **HBRC**1, because its proton affinity, 171 kcal mol^{-1} [23], lies in between that of the **AN**R1 radical $CH_2{=}C^{\cdot}{-}CN$ at C$^{\cdot}$ and at N, 167 and 185 kcal mol^{-1} respectively [8]. Indeed, the energy diagram of Scheme 3 indicates that the HCN component of **HBRC**1 may rather easily abstract the C–H hydrogen of **AN** and transfer it to the N atom to form **HBRC**3, which loses HCN to yield **AN**1.

In the same vein, PTC within **HBRC**2 leads to **HBRC**4, which dissociates into **AN**2 + HCN.

Experimental evidence that PTC indeed occurs in the interaction of **AN** with HCN in the hexapole reaction chamber of our tandem mass spectrometer is presented in Fig. 1d. It is seen that this CID spectrum of *m/z* 53 ions **AN** which have interacted with HCN is quite different from that obtained of **AN** ions transmitted through the empty hexapole, Fig. 1c. *Prima facie*, it looks as if **AN** has been transformed into **AN**2: the spectra of Figs. 1b and d are very similar. However, the *m/z* 40 tell-tale peak for loss of CH from **AN**2 is conspicuously low in Fig. 1d, indicating that its elusive isomer **AN**1 discussed in the previous section, is the predominant reaction product.

The picture that emerges from this theoretical and experimental study of the **AN**/HCN dimer ions is that pyrimidine formation via cyclization as well as protonation is energetically possible but does not compete with the more favoured HCN catalyzed isomerization of **AN**.

Acknowledgements

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