The formation of the stable radicals ${}^{\bullet}CH_2CN$, $CH_3{}^{\bullet}CHCN$ and ${}^{\bullet}CH_2CH_2CN$ from the anions ${}^{-}CH_2CN$, $CH_3{}^{-}CHCN$ and ${}^{-}CH_2CH_2CN$ in the gas phase. A joint experimental and theoretical study

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Received 21st February 2006, Accepted 27th April 2006
First published as an Advance Article on the web 18th May 2006
DOI: 10.1039/b602621d

Franck–Condon one-electron oxidation of the stable anions ${}^{-}CH_2CN$, $CH_3{}^{-}CHCN$ and ${}^{-}CH_2CH_2CN$ (in the collision cell of a reverse-sector mass spectrometer) produce the radicals ${}^{\bullet}CH_2CN$, $CH_3{}^{\bullet}CHCN$ and ${}^{\bullet}CH_2CH_2CN$, which neither rearrange nor decompose during the microsecond duration of the neutralisation–reionisation experiment. Acetonitrile (CH_3CN) and propionitrile (CH_3CH_2CN) are known interstellar molecules and radical abstraction of these could produce energised ${}^{\bullet}CH_2CN$ and $CH_3{}^{\bullet}CHCN$, which might react with $NH_2{}^{\bullet}$ (a known interstellar radical) on interstellar dust or ice surfaces to form NH_2CH_2CN and $NH_2CH(CH_3)CN$, precursors of the amino acids glycine and alanine.

Introduction

A knowledge of the mode of formation of amino acids is important for the understanding of the origin of life in our Galaxy.[1–3] Amino acids have been found in meteorites[4–8] and they have also been found following electrical discharge in systems modelling the atmosphere of primordial Earth,[9,10] and following UV irradiation of interstellar ice models.[11,12] The search for the simplest amino acid, glycine, in interstellar dust clouds, circumstellar envelopes, interstellar ice and comets has been ongoing for more than two decades with mixed initial success.[13–21] Perhaps the identification of interstellar glycine has been made difficult because it likely that amino acids are destroyed by UV photolysis in interstellar clouds.[22,23] In spite of this, the detection of glycine (using rotational spectroscopy) has recently been claimed in the hot molecular cores Sagittarius B2, Orion KL and W5.[24,25] This, together with the detection of some 120 other molecules in stellar regions,[22,26–28] suggests that interstellar molecules could have played an important role of the prebiotic chemistry of Earth.

It has been suggested that amino acids in some meteorites[29] and also in interstellar clouds[30,31] may be formed by the Strecker reaction [$CH_2O + NH_3 + HCN \rightarrow NH_2CH_2CN + H_2O \rightarrow NH_2CH_2CO_2H$[32] ($CH_2O$, NH_3 and HCN are all found in interstellar regions)], or the Tiemann (cyanhydrin) modification of the Strecker process.† Proposals of synthetic routes to glycine in interstellar regions are numerous. Apart from the Strecker reaction, other proposals are that glycine may be formed from formic acid[22,34–37] (particularly in interstellar ice) by reaction with CH_2NH,[34] $CH_3NH_2{}^{+}$ [35] or NH_2CH_2OH[22,37] (*e.g.* $NH_2CH_2OH_2{}^{+} + HCO_2H \rightarrow NH_2CH_2CO_2H_2{}^{+} + H_2O$), and from the reaction between acetic acid and ${}^{+}NH_2OH$.[38] However, utilisation of amines as building blocks for interstellar amino acids has recently been questioned.[39] In addition, it has been shown that the reactions between CH_2NH^{+} and the interstellar molecules HCN or HNC are energetically unfavourable.[40] A recent suggestion is that glycine may be formed in interstellar ice by the multistep process $CH_2NH_2 + CO_2 + H \rightarrow NH_2CH_2CO_2H$.[41]

Two proposals that are particularly interesting in the context of this paper are (i), glycine may be formed by radical coupling reactions (on dust particles or in interstellar ice),[42] and (ii), NH_2CH_2CN may be the precursor of interstellar glycine; but formed from cyanogen[43] (NCCN, a species not yet detected in interstellar regions) rather than the Strecker process. The proposal of NH_2CH_2CN as a glycine precursor is plausible on several grounds: namely, (i) amino acids are much less stable to UV irradiation in interstellar regions than nitriles[22] (which are abundant in interstellar regions[26–28] even though NH_2CH_2CN has not itself been detected), (ii) nitriles should be readily hydrolysed to carboxylic acids in interstellar ice in exothermic reactions with only small barriers (barrier calculated to be *ca.* 6 kJ mol^{-1} [40]). Finally, the analogous $NH_2CH(R)CN$ species could, in principle, produce other amino acids in interstellar regions (*e.g.* $R = CH_3$ would give the alanine precursor).

If radical reactions produce amino acid precursors in interstellar regions, then $CH_3{}^{\bullet}CHCN$ could be a precursor of alanine. How might this radical be formed in interstellar clouds or ice? Balucani *et al.*[44] have described the crossed beam reaction between the cyano radical and ethylene to produce vinyl cyanide (all known interstellar molecules), and have probed the reaction coordinate of this reaction using the B3LYP level with the 6-311G(d,p) basis set. A simplified version of these results is shown in Fig. 1, and our data (Table 1) for the ${}^{\bullet}CH_2CH_2CN$ to $CH_3{}^{\bullet}CHCN$ rearrangement are qualitatively similar to those shown in Fig. 1. The reaction between the cyano radical and ethylene gives ${}^{\bullet}CH_2CH_2CN$ with 232 kJ mol^{-1} of excess energy at the level of theory used for the calculation of Balucani *et al.*[44] The first formed radical may rearrange to $CH_3{}^{\bullet}CHCN$ or dissociate to $CH_2{=}CHCN$ as shown in Fig. 1. Nitrile to isonitrile isomerisations are energetically unfavourable in comparison with the two reactions described above.[44] The authors state that since ${}^{\bullet}CH_2CH_2CN$ and $CH_3{}^{\bullet}CHCN$ are formed with

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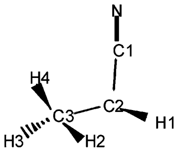
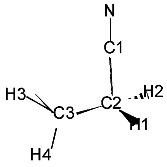
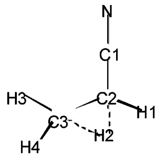
† The acid hydrolysis of NH_2CH_2CN to glycine involves protonation of the nitrile group, however the amino group will be preferentially protonated: the relative proton affinities of the NH_2 and CN in aminoacetonitrile are 820 and 780 kJ mol^{-1} respectively in the gas phase.[33]

Table 1 Energies and geometries for doublet neutrals

	 ^{2}**1**	 ^{2}**2**	 **Ts 1/2**
Symmetry	C_1	C_1	C_1
Energy/Hartree[a]	−170.91225	−170.89852	−170.84091
Relative energy/kJ mol^{-1}	0	+36	+190
Dipole moment/Debye[b]	4.15	4.02	
Electron affinity/eV[a]	1.12	1.50	
Bond length/Å or angle/°[b]			
NC1	1.177	1.161	1.169
C1C2	1.389	1.468	1.417
C2C3	1.497	1.499	1.490
C1C3	2.539	2.482	2.547
H1C2	1.087	1.104	1.086
H2C2		1.101	1.265
H2C3	1.099		1.354
H3C3	1.099	1.083	1.083
H4C3	1.093	1.085	1.083
NC1C2	179.8	179.7	178.3
C1C2C3	123.2	113.5	122.3
C1C2H1	117.3	107.8	117.5
C1C2H2		108.1	114.4
C2C3H2	110.6		
C2C3H3	111.9	121.5	119.7
C2C3H4	110.6	119.0	118.5
NC1C2C3	0.0	28.0	−85.1
NC1C2H1	180.0	−95.4	112.5
NC1C2H2		151.4	−18.5
C1C2C3H3	0.0	−9.8	5.0
C1C2C3H4	−121.1	173.7	−163.4

[a] CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory including zero-point energy (B3LYP/6-31+G(d). [b] B3LYP/6-31+G(d) level of theory.

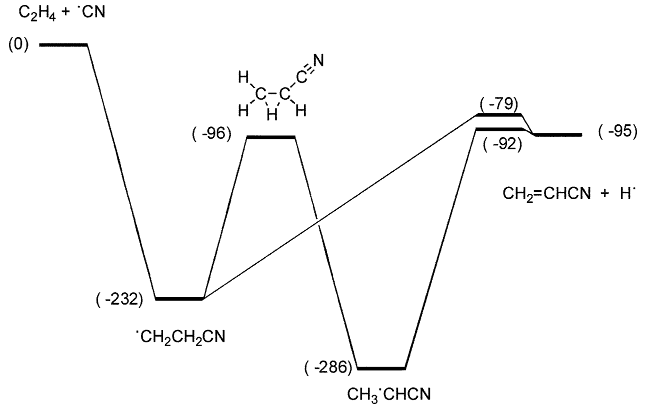


Fig. 1 Reaction coordinate profile of the reaction between the cyano radical and ethylene at the B3LYP/6-311G(d,p) level of theory. Modified from ref. 44. The relative energies obtained from our calculations at the CCSD(T) aug-cc-pVDZ//B3LYP/6-31G+(d) level of theory are $CH_3{}^{\bullet}CHCN$ (0 kJ mol^{-1}), transition state (+190 kJ mol^{-1}) and $^{\bullet}CH_2CH_2CN$ (+36 kJ mol^{-1}) [see Table 1].

excess energy in this reaction sequence, these two radicals will be short lived and should not be precursors in interstellar chemical reactions.

This paper considers the possibility that $^{\bullet}CH_2CN$ and $CH_3{}^{\bullet}CHCN$ may be precursors of interstellar glycine and alanine. The formation of these radicals (together with $^{\bullet}CH_2CH_2CN$) by charge stripping of the corresponding anions in the gas phase is investigated.

Results and discussion

The major question addressed in this paper is whether the radicals $^{\bullet}CH_2CN$[45] and $CH_3{}^{\bullet}CHCN$[44] could be intermediates in the formation of glycine and alanine in interstellar media. In principle, the reactions between $NH_2{}^{\bullet}$ and $^{\bullet}CH_2CN$ and $CH_3{}^{\bullet}CHCN$ in the gas phase will give NH_2CH_2CN and $NH_2CH(CH_3)CN$ in exothermic and barrierless reactions.‡ The problem is that all three radicals will be formed with excess energy, and so each reaction will require a third body (either interstellar dust or ice) to remove the excess energy of formation of radicals and products, unless these are deactivated radiatively. The possibility of $^{\bullet}NH_2$ reacting on dust surfaces has already been raised,[46] and $^{\bullet}NH_2$ has been

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‡ It has also been suggested that, in principle, glycine could be made by the reaction between $NH_2{}^{\bullet}$ and acetic acid.[42] Even if this is feasible, it is likely that the amino acid would be largely destroyed in interstellar clouds by ultraviolet irradiation.

tentatively assigned as an interstellar molecule within Sagittarius B2[47] and Orion KL.[48]

Balucani *et al.*[44] have proposed that if $CH_3{}^{\bullet}CHCN$ is formed by the process shown in Fig. 1, its excess energy of formation (286 kJ mol^{-1}) means that this radical will be short lived and not be a precursor in interstellar chemical reactions. This presupposes that $^{\bullet}CH_2CH_2CN$ is the precursor of $CH_3{}^{\bullet}CHCN$ in the interstellar media. However, $CH_3{}^{\bullet}CHCN$ may be produced by an alternative route to that shown in Fig. 1. Propionitrile is a known interstellar molecule:[28] perhaps propionitrile may undergo hydrogen atom abstraction to yield $CH_3{}^{\bullet}CHCN$? For example, the reactions $CH_3CH_2CN + H^{\bullet} \rightarrow H_2 + CH_3{}^{\bullet}CHCN$ and $CH_3CH_2CN + HO^{\bullet} \rightarrow H_2O + CH_3{}^{\bullet}CHCN$ have calculated ΔH values of -60 and -120 kJ mol^{-1} respectively (individual values from the NIST WebBook, also ΔH°_f of $CH_3{}^{\bullet}CHCN$ is 210 ± 10 kJ mol^{-1} [49]). Even the reaction $Cl^{\bullet} + CH_3CN \rightarrow HCl + {}^{\bullet}CH_2CN$ is exothermic, but the presence of a reactant like transition state results in a slow rate of 2×10^{-15} cm^3 molecule^{-1} s^{-1} for this process.[50,51]

The formation of radicals from the corresponding anions

Previously, we have used the neutralisation–reionisation procedure ($^-NR^+$)[52] to allow the production and study of transient species of relevance in interstellar chemistry from anions of known bond connectivity.[53] In this case we first seek to make $^-CH_2CN$, $CH_3{}^-CHCN$ and $^-CH_2CH_2CN$ by unequivocal routes and determine whether these anions are stable under the conditions used to effect the one-electron Franck–Condon oxidations. The three anions were made by either deprotonation reactions [eqn (1) and (2)] or by the S_N2 (Si) process[54] in the ion source of the mass spectrometer. The labelled species $^-CD_2CN$, $CH_3{}^-CDCN$ and $^-CH_2CD_2CN$ were formed by analogous reactions.

$$HO^- + CH_3CN \rightarrow {}^-CH_2CN + H_2O \qquad (1)$$

$$HO^- + CH_3CH_2CN \rightarrow CH_3{}^-CHCN + H_2O \qquad (2)$$

$$F^- + (CH_3)_3SiCH_2CH_2CN \rightarrow {}^-CH_2CH_2CN + (CH_3)_3SiF \qquad (3)$$

(a) The $^{\bullet}CH_2CN$ system. The spectra of $^-CH_2CN$ and the labelled species $^-CD_2CN$ are considered first to illustrate the applicability of the neutralisation–reionisation method for this system. The collision-induced negative ion spectra of $^-CH_2CN$ and $^-CD_2CN$ show the following peaks: [m/z (loss) abundance]; $^-CH_2CN$: 40 (parent) 100%, 39 ($H^{\bullet}$) 1, 38 (H_2) 1 and 26 (CH_2) 1. $^-CD_2CN$: 42 (parent) 100%; 40 ($D^{\bullet}$) 1; 38 (D_2) 1 and 26 (CD_2) 0.5%. These fragmentations are diagnostic of anions with bond connectivities CH_2CN and CD_2CN. This means that $^-CH_2CN$ is an appropriate precursor for radical $^{\bullet}CH_2CN$ since the anion is stable under the collision conditions used for the $^-NR^+$ experiment. The charge-reversal spectrum ($^-CR^+$, synchronous two electron oxidation of the anion to the corresponding cation),[55] and the neutralisation–reionisation spectrum ($^-NR^+$, sequential one-electron oxidation to the neutral followed by one electron oxidation to the cation)[52] of $^-CD_2CN$ are shown in Fig. 2. The two spectra are very similar, with both showing partial D rearrangement of the decomposing cation $^+CD_2CN$ [*e.g.* losses of C and CD (rearrangement) and CD_2 (no rearrangement)]. The observation that both spectra are very similar [but with partial (and identical) extents of rearrangement] indicates that (i) $^{\bullet}CH_2CN$ and $^{\bullet}CD_2CN$ are stable for the duration (one microsecond) of the $^-NR^+$ experiment, and (ii) it is the first formed cation which is undergoing rearrangement.

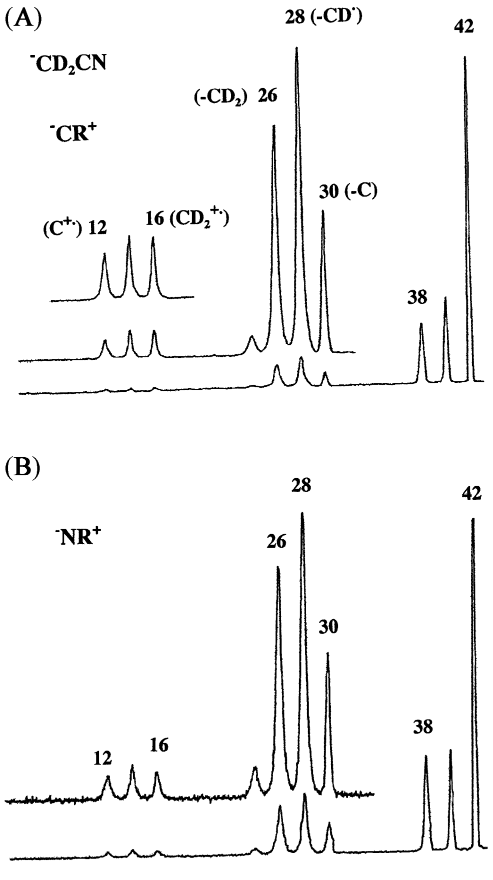
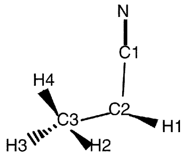
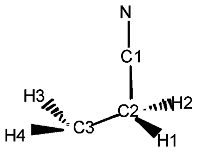
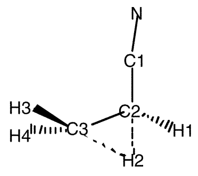


Fig. 2 The $^-CR^+$ (**A**) and $^-NR^+$ (**B**) spectra of $^-CD_2CN$. VG ZAB 2HF mass spectrometer. For experimental details see the Experimental section.

(b) The $CH_3{}^{\bullet}CHCN$ and $^{\bullet}CH_2CH_2CN$ systems. These two systems are considered together because Balucani *et al.* have suggested that $CH_3{}^{\bullet}CHCN$ may be formed from $^{\bullet}CH_2CH_2CN$ in the reaction between the cyano radical and ethylene.[44] The situation concerning the two precursor anions may be more complex than that considered above for deprotonated acetonitrile. It has been shown previously that some β-ethyl anions rearrange to more stable isomers when energised (*e.g.* $^-CH_2CH_2CH{=}CH_2 \rightarrow {}^-CH_2CH{=}CHCH_3$[56,57]). Thus it is possible that $^-CH_2CH_2CN$ may rearrange to $CH_3{}^-CHCN$ under the collisional conditions required to effect the Franck–Condon one-electron oxidation of $^-CH_2CH_2CN$ to $^{\bullet}CH_2CH_2CN$. However, it was shown earlier,[58] that the decomposition of $^-CH_2CH_2CN$ to ethylene and the cyano radical is more favourable thermodynamically than the rearrangement of $^-CH_2CH_2CN$ to $CH_3{}^-CHCN$. We consider, further, the possibility of this rearrangement from both experimental and theoretical viewpoints.

The singlet states of $CH_3{}^-CHCN$ and $^-CH_2CH_2CN$ are more stable than the corresponding triplets by 173 and 127 kJ mol^{-1} (respectively) at the CCSD(T) aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Thus we have considered only the reaction coordinate on the singlet potential surface (see Table 2). Singlet anion $CH_3{}^-CHCN$ is the more stable of the two isomeric anions by 81 kJ mol^{-1} with the barrier for conversion of $^-CH_2CH_2CN$

Table 2 Energies and geometries for singlet anions

	 $^{1}1^{-}$	 $^{1}2^{-}$	 Ts $^{1}1^{-}/^{1}2^{-}$
Symmetry	C_1	C_1	C_1
Energy/Hartree[a]	−170.95351	−170.92274	−170.86399
Rel. energy/kJ mol^{-1}	0	+81	+235
Dipole moment/Debye[b]	4.32	4.11	
Bond length/Å or bond angle/°[b]			
NC1	1.192	1.171	1.182
C1C2	1.387	1.500	1.411
C2C3	1.515	1.534	1.600
C1C3	2.516	2.592	2.645
H1C2	1.091	1.102	1.090
H2C2		1.102	1.237
H2C3	1.102		1.371
H3C3	1.116	1.105	1.093
H4C3	1.102	1.105	1.101
NC1C2	177.9	174.9	174.9
C1C2C3	120.1	117.3	122.8
C1C2H1	116.6	105.6	115.8
C1C2H2		105.6	129.2
C2C3H2	110.7		
C2C3H3	116.0	109.6	109.1
C2C3H4	111.5	109.6	114.4
NC1C2C3	71.4	0.0	70.8
NC1C2H2		−124.2	0.2
C1C2C3H4	−48.1	59.0	103.1
NC1C2H1	−136.9	124.2	−140.3
C1C2C3H3	72.9	−59.0	−23.5
C1C2C3H2	−166.2		

[a] CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory including zero-point energy (B3LYP/6-31+G(d). [b] B3LYP/6-31+G(d) level of theory.

Table 3 CID Spectra of $CH_3{}^-CHCN$ and $^-CH_2CH_2CN$ and labelled analogues *m*/*z* (loss) relative abundance (%)

$CH_3{}^-CHCN$	54 (parent) 100%; 53 (H) 0.1; 52 (H_2) 0.3; 39 ($CH_3{}^{\bullet}$) 0.2; 26 (C_2H_4) 0.2
$CH_3{}^-CDCN$	55 (parent) 100%, 54 (H) 0.1; 52 (HD) 0.3; 39 ($CH_3{}^{\bullet}$) 0.2; 26 (C_2H_3D) 0.2
$^-CH_2CH_2CN$	54 (parent) 100%; 53 (H) 2; 52 (H_2) 0.3; 26 (C_2H_4) 0.2
$^-CH_2CD_2CN$	56 (parent) 100%; 55 (H) 0.5; 54 (H_2/D) 0.1; 53 (HD) 0.1; 52 (D_2) 0.1; 26 ($C_2H_2D_2$) 0.2

to $CH_3{}^-CHCN$ being 153 kJ mol^{-1}. The only examples of isomerisation of anions that we have observed previously occur when the interconversion barrier is $\leq$ 55 kJ mol^{-1}.[53] The collision induced (CID) spectra of these anions and their labelled analogues are listed in Table 3. Peaks arising from dissociation are minor in comparison with the abundances of the parent anions. The loss of CH_2 from $^-CH_2CH_2CN$ and $CH_3{}^{\bullet}$ from $CH_3{}^-CHCN$ are diagnostic of these structures. Thus theory and experiment suggest that the two anions are stable when formed by the reactions shown in eqn (2) and (3), in spite of earlier findings that other substituted β-ethyl anions may be converted readily to more stable isomers.[56,57] This is also consistent with the earlier findings of Kass[58] that the rearrangement is less favourable than dissociation of $^-CH_2CH_2CN$. Thus, the two anions should be appropriate precursors for the production of $^{\bullet}CH_2CH_2CN$ and $CH_3{}^{\bullet}CHCN$.

The neutrals $CH_3{}^{\bullet}CHCN$ and $^{\bullet}CH_2CH_2CN$ should be formed from $CH_3{}^-CHCN$ and $^-CH_2CH_2CN$ with Franck–Condon energies (the excess energy of the neutral with the anion geometry compared with that of the neutral at the potential minimum) of 9 and 35 kJ mol^{-1} respectively at the level of theory used in this study. These energies are not, by themselves, sufficient to effect rearrangement or decomposition of the neutral radicals (see *e.g.* Fig. 1).

The $^-CR^+$ and $^-NR^+$ mass spectra of $CH_3{}^-CHCN$ and $^-CH_2CH_2CN$ are recorded in Figs. 3 and 4 respectively, while the analogous spectra of the two labelled derivatives are listed in Table 4. The key points to note are (i) the $^-CR^+$ and $^-NR^+$ spectra of $CH_3{}^-CHCN$ are very similar, as are those of $^-CH_2CH_2CN$, but (ii) the spectra of the two isomers are different. The fragmentations in the spectra are quite complex but are consistent with the expected structures of the two radicals. For example there is major peak in Fig. 3 due to loss of $CH_3{}^{\bullet}$ accompanied by a sequential loss of ($CH_3{}^{\bullet}$ + $H^{\bullet}$) [consistent with a structure of $CH_3{}^{\bullet}CHCN$] while Fig. 4 shows losses of CH_2 together

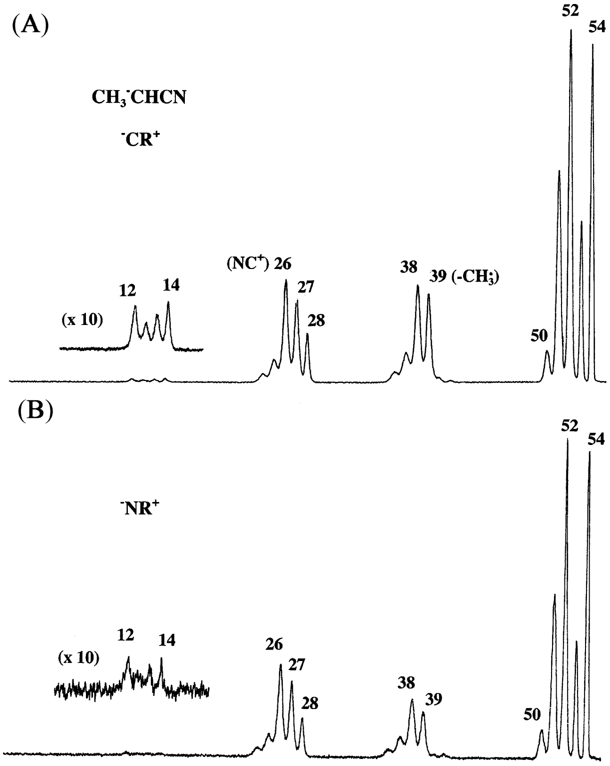


Fig. 3 The $^-CR^+$ (**A**) and $^-NR^+$ (**B**) spectra of $CH_3{}^-CHCN$. VG ZAB 2HF mass spectrometer. For experimental details see Experimental section.

with (CH_2 + H$^•$) and (CH_2 + H_2) [consistent with structure $^•CH_2CH_2CN$]. The spectra of the labelled analogues (Table 4) show that there is minor H–D rearrangement occurring within $CH_3{}^+CDCN$ and $^+CH_2CD_2CN$. Notwithstanding this, the spectra listed in Table 4 are consistent with those reproduced in Figs. 3 and 4. The observation that there is partial rearrangement occurring following formation of parent cations in both Figs. 3 and 4,§ and that the $^-NR^+$ and $^-CR^+$ spectra in each of these figures are very similar, means that neither radical rearranges or dissociates to a measurable extent during the microsecond duration of the NR experiment. These experimental findings are in accord with our calculations (Table 1) and those of Balucani *et al.*[44]

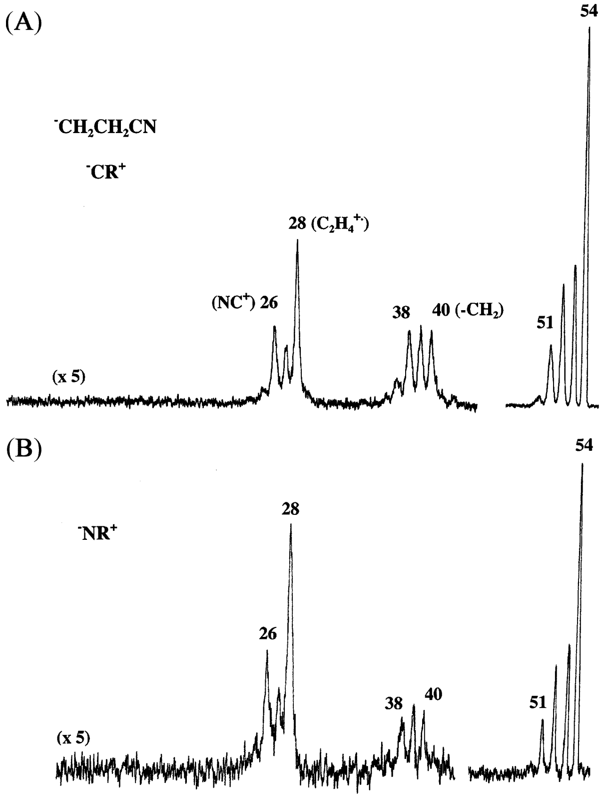


Fig. 4 The $^-CR^+$ (**A**) and $^-NR^+$ (**B**) spectra of $^-CH_2CH_2CN$. VG ZAB 2HF mass spectrometer. For experimental details see Experimental section.

Conclusions

(i) The anions $^-CH_2CN$, $CH_3{}^-CHCN$ and $^-CH_2CH_2CN$ have been made from precursors of known bond connectivity. The anions are stable and do not rearrange when energised by collisions in the first collision cell of the mass spectrometer.

(ii) Franck–Condon vertical one-electron oxidation converts each of the three anions to the corresponding doublet radical: $^•CH_2CN$, $CH_3{}^•CHCN$ or $^•CH_2CH_2CN$. These radicals are stable; there is no evidence to indicate that they rearrange or dissociate during the microsecond duration of the neutralisation–reionisation experiment.

Experimental

A Mass spectrometric experiments

All experiments were performed with a VG ZAB 2HF two-sector mass spectrometer of BE configuration (B stands for

Table 4 The $^-CR^+$ and $^-NR^+$ spectra of $CH_3{}^-CDCN$ and $^-CH_2CD_2CN$ *m*/*z* (relative abundance)

$CH_3{}^-CDCN$
$^-CR^+$ 55 parent (100%), 54(42), 53(86), 52(74), 51(46), 50(8), 40(35), 39(11), 38(33), 37(6), 36(3), 29(11), 28(22), 27(34), 26(21), 25(8), 24(1), 15(0.5), 14(0.5), 12(0.3)
$^-NR^+$ 55 parent (100%), 54(45), 53(89), 52(73), 51(46), 50(10), 40(38), 39(13), 38(36), 37(5), 36(2), 29(14), 28(25), 27(36), 26(24), 25(9), 24(2), 15(0.3), 14 (0.2), 12(0.2)
$^-CH_2CD_2CN$
$^-CR^+$ 56 parent (46%), 55(54), 54(100), 53(3), 52(1), 42(5), 41(8), 40(8), 38(2), 30(16), 29(26), 28(35), 26(14)
$^-NR^+$ 56 parent (51%), 55(47), 54(100), 53(4), 52(1), 42(7), 41(10), 38(2), 30(15), 29(25), 28(38), 26(12)

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§ A reviewer has suggested that some consideration of cation decompositions could be provided here. Cation reactions are not part of the major thrust of this paper, but literature is available concerning C_2H_2N[59,60] and C_3H_4N[59] cationic systems.

magnetic and E for electric sector), which has been described previously.[61] In summary, the precursor anions $^{-}CH_2CN$ and $Me^{-}CHCN$ were made by the reaction between HO^- (from H_2O[62]) and CH_3CN and CH_3CH_2CN in the source of the mass spectrometer. The corresponding D labelled compounds CD_3CN and CH_3CD_2CN were treated with DO^- (from D_2O) in the ion source to yield $^{-}CD_2CN$ and $CH_3{}^{-}CDCN$ respectively. The anions $^{-}CH_2CH_2CN$ and $^{-}CH_2CD_2CN$ were formed in the ion source by the reaction of F^- (from SF_6[54,63]) with $(CH_3)_3SiCH_2CH_2CN$ and $(CH_3)_3SiCH_2CD_2CN$ respectively. The neutral precursors in these reactions were introduced *via* the direct probe in which a capillary containing the sample was drawn out to a very fine aperture, allowing for a slow release of vapour pressure to give a measured pressure in the source housing of 5×10^{-6} Torr. The direct probe and the ion source were heated to 50 °C, conditions under which the nitriles are stable. The reagents in the ion source, HO^- (from H_2O), DO^- (from D_2O) or F^- (from SF_6) were added to give a pressure of 10^{-5} Torr in the source housing: estimated total pressure in the ion source, 10^{-1} Torr. Anions were accelerated to 7 keV translational energy and mass selected by means of the magnet. For collisional induced (CID) dissociations, the ions were collided in the first of two tandem collision cells (between B and E) with helium at 80% transmission (T) of the incident beam; these conditions approximate single-collision conditions.[64]

In neutralisation–reionisation experiments ($^{-}NR^{+}$)[52] the anions were neutralised by high-energy collisions with molecular oxygen (80% T) in the first of two collision cells located in the field-free region between B and E. Unreacted ions were deflected away from the beam of neutral species by applying a voltage of 300 V on a deflector electrode located between the two collision chambers. Reionisation of the neutrals to cations occurred in the second cell following collision with oxygen (80% T). The resulting spectra were obtained by scanning E (with the polarity of the sector voltage reversed to allow the passage of positive ions). Charge reversal spectra ($^{-}CR^{+}$) of the anions to cations[55] were obtained by colliding the ion beam with oxygen (80% T) in the first collision cell, and measuring the spectrum as described above for the $^{-}NR^{+}$ method. Under these conditions, the $^{-}CR^{+}$ process can be treated as a vertical, two-electron oxidation occurring through a single step at a time scale of a few femtoseconds, although some species might undergo multiple collisions.

B Precursor molecules

Acetonitrile, D_3-acetonitrile and propionitrile were commercial products. CH_3CD_2CN was obtained by allowing propionitrile to react with D_2O in ion source of the instrument.[62] 3-Trimethylsilylpropionitrile was prepared by a reported procedure.[58] The labelled derivative $(CH_3)_3SiCH_2CD_2CN$ was made by the same procedure[58] except that D_3-acetonitrile is used instead of acetonitrile [$D_2 = 99\%$ (by NMR)].

C Theoretical methods

Geometry optimisations were carried out with the Becke 3LYP method[65] using the 6-31+D(d) basis set within the Gaussian 98 (revision A9) suite of programs.[66] Stationary points were characterised as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition state were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were then scaled by 0.9804[67] and used as zero-point correction for the electronic energies. More accurate energies for the B3LYP geometries were determined using the CCSD(T) method[68] together with the Dunning aug-cc-pVDZ basis set.[69]

Acknowledgements

We thank the Australian Research Council for funding our negative ion studies and for providing a research associate stipend to MF. We acknowledge a generous allocation of time on the APAC alpha server supercomputer (Australian National University, Canberra).

References

1 L. E. Snyder, *Origins Life Evol. Biosphere*, 1997, **27**, 115.
2 ed. A. Brack, *The molecular origin of life*. Cambridge University Press, New York, 1998.
3 H. S. Zhu and J. J. Ho, *J. Phys. Chem. A*, 2004, **108**, 3798.
4 J. R. Cronin and S. Pizzarello, *Adv. Space Res.*, 1983, **3**, 1983.
5 J. R. Cronin and S. Chang, in *Chemistry of Life's Origins*, ed. J. M. Greenberg, V. Pirronello and C. Mendoza-Gomez, eds., NATO ASI, 1993, pp. 209–258, Kluwer, Dordrecht.
6 S. P. Walch and E. L. O. Bakes, *Chem. Phys. Lett.*, 2001, **346**, 267.
7 D. E. Woon, *Astrophys. J.*, 2002, **571**, L177.
8 G. Botta, D. P. Glavin, G. Kminek and J. L. Bala, *Origins Life Evol. Biosphere*, 2002, **32**, 143.
9 S. L. Miller, *Science*, 1953, **117**, 528.
10 Y. Takano, A. Ohashi, T. Kaneko and K. Kobayashi, *Appl. Phys. Lett.*, 2004, **84**, 1410.
11 M. P. Bernstein, J. P. Dworkin, S. A. Sandford, G. W. Cooper and L. J. Allamandola, *Nature*, 2002, **416**, 401.
12 G. M. Munoz Caro, U. L. Melerhenrich, W. A. Schutte, B. Barbler, A. A. Segovia, H. Rosenbaure, W. H.-P. Thiemann, A. Brack and J. M. Greenberg, *Nature*, 2002, **416**, 403.
13 R. D. Brown, P. D. Godfrey and J. W. V. Storey, *Mon. Not. R. Astron. Soc.*, 1979, **186**, 5P.
14 J. M. Hollis, L. E. Snyder, R. D. Suenram and F. J. Lovas, *Astrophys. J.*, 1980, **241**, 1001.
15 L. E. Snyder, J. M. Hollis, F. J. Suenram, F. J. Lovas, L. W. Brown and D. Buhl, *Astrophys. J.*, 1983, **268**, 123.
16 I. I. Berulis, S. A. Sandford and L. J. Allamandole, *Sov. Astron. Lett.*, 1985, 251.
17 ed. M. Guelin and J. Cernicharo, in G. Winnewisser and T. Arstrong, *Physics and Chemistry of Interstellar Molecular Clouds*, Springer-Verlag, Berlin, 1989, p. 337.
18 F. Combes, N.-Q. Rieu and G. Wlodarszak, *Astron. Astrophys.*, 1996, **308**, 618.
19 C. Ceccarelli, L. Loinard, A. Castets, A. Faure and B. Lefloch, *Astron. Astrophys.*, 2000, **326**, 1122.
20 J. M. Hollis, J. A. Pedalty, L. E. Snyder, P. R. Jewell, F. J. Lovas, P. Palmer and S. Y. Lie, *Astrophys. J.*, 2003, **588**, 353.
21 J. Crovisier, D. Bockelee-Morvan, P. Colom, N. Biver, D. Despois and D. C. Lis, *Astron. Astrophys.*, 2004, **418**, 1141.
22 P. Ehrefreund, M. P. Berstein, J. P. Dworkin, S. A. Sandford and L. J. Allamandola, *Astrophys. J.*, 2001, **550**, L95.
23 M. P. Bernstein, S. F. M. Ashbourne, S. A. Sandford and L. J. Allamandola, *Astrophys. J.*, 2004, **601**, 365.
24 S. B. Charley, P. Ehrenfreund and Y.-J. Kuan, *Spectrochim. Acta, Part A*, 2001, **57**, 685.
25 Y.-J. Kuan, S. B. Charnley, H. C. Huang, W. L. Tseng and Z. Kisiel, *Astrophys. J.*, 2003, **593**, 848.
26 D. Smith and P. Spanel, *Mass Spectrom. Revs.*, 1995, **14**, 225; G. Winnewisser and C. Kramer, *Space Sci. Rev.*, 1999, **90**, 181.
27 S. B. Charley, P. Ehrenfreund and Y.-J. Kuan, *Spectrochim. Acta, Part A*, 2001, **57**, 685.

28 A. Wootten, http://www.cv.nrao.edu/~awootten/allmols.html.

29 O. Botta, D. P. Glavin, G. Kminek and J. L. Bada, *Origins Life Evol. Biosphere*, 2002, **32**, 143.

30 R. Arnaud, C. Adamo, M. Cossi, A. Milet, Y. Valleé and V. Barone, *J. Am. Chem. Soc.*, 2000, **122**, 324.

31 V. A. Basiuk, *J. Phys. Chem. A*, 2001, **105**, 4252.

32 A. Strecker, *Liebigs Ann. Chem.*, 1850, **75**, 27.

33 G. Bouchoux, J.-C. Guillemin, N. Lemahieu and T. B. McMahon, *Rapid Commun. Mass Spectrom.*, 2006, **20**, 1187.

34 D. E. Woon, *Int. J. Quantum Chem.*, 2002, **88**, 226.

35 A. Largo, P. Redondo and C. Barrientos, *Int. J. Quantum Chem.*, 2004, **98**, 355.

36 H. M. Boechat-Roberty, S. Pilling and A. C. F. Santos, *Astron. Astrophys.*, 2005, **438**, 915.

37 M. T. Feldmann, S. L. Widicus, G. A. Blake, D. R. Kent and W. A. Goddard, *J. Chem. Phys.*, 2005, **123**, 34304.

38 V. Biagojevic, S. Petrie and D. K. Bohme, *Mon. Not. R. Astron. Soc.*, 2003, **339**, L7.

39 D. M. Jackson, N. J. Stibrich, N. G. Adams and L. M. Badcock, *Int. J. Mass Spectrom.*, 2005, **243**, 115.

40 S. P. Walch and E. L. O. Bates, *Chem. Phys. Lett.*, 2001, **346**, 267.

41 P. D. Holton, C. J. Bennett, Y. Osanuna, N. J. Mason and R. I. Kaiser, *Astrophys. J.*, 2005, **626**, 940.

42 W. H. Sorrell, *Astrophys. J.*, 2001, **555**, L129.

43 V. A. Basiuk and Y. Kobayashi, *Int. J. Quantum Chem.*, 2004, **99**, 99.

44 N. Balucani, O. Asvany, A. H. H. Chang, S. H. Lin, Y. T. Lee and R. I. Kaiser, *J. Chem. Phys.*, 2000, **113**, 8643.

45 C. J. Parkinson, P. M. Mayer and L. Radom, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2305; R. D. Lafluer, B. Szatary and T. Baer, *J. Phys. Chem. A*, 2000, **104**, 1450; B. S. Wang, H. Hou and Y. S. Gu, *J. Phys. Chem. A*, 2001, **105**, 1546; D. J. Henry, C. J. Parkinson and L. Radom, *J. Phys. Chem. A*, 2002, **106**, 7927.

46 J. M. Hollis and E. Churchwell, *Astrophys. J.*, 2001, **551**, 83.

47 J. R. Goicoechea, N. J. Rodriquez-Ferandez and J. Cernicharo, *Astrophys. J.*, 2004, **600**, 214.

48 C. Comito, P. Schilke, T. G. Phillips, D. C. Lis, F. Motte and D. Mehringer, *Astron. J. Suppl. Ser.*, 2005, **156**, 127.

49 K. D. King and R. D. Goddard, *J. Am. Chem. Soc.*, 1975, **97**, 4504.

50 M. J. Kurylo and G. L. Knable, *J. Phys. Chem.*, 1984, **88**, 3305.

51 K. Pei and H. Li, *J. Mol. Struct. (THEOCHEM)*, 2004, **67**, 677.

52 C. Wesdemiotis and F. W. McLafferty, *Chem. Rev.*, 1987, **87**, 485; D. V. Zagorevskii and J. L. Holmes, *Mass Spectrom. Rev.*, 1994, **13**, 38; N. Goldberg and H. Schwarz, *Acc. Chem. Res.*, 1994, **13**, 133; C. A. Shalley, G. Hornung, D. Schröder and H. Schwarz, *Int. J. Mass Spectrom. Ion Processes*, 1998, **172**, 181; D. V. Zagorevskii and J. L. Holmes, *Mass Spectrom. Rev.*, 1999, **18**, 87.

53 S. Dua, S. J. Blanksby, S. Peppe, A. M. McAnoy and J. H. Bowie, *Curr. Org. Chem.*, 2003, **7**, 1543.

54 C. H. DePuy, V. Bierbaum, L. A. Flippin, J. J. Grabowski, G. K. King, R. J. Smitt and S. A. Sullivan, *J. Am. Chem. Soc.*, 1980, **102**, 5012.

55 J. H. Bowie and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **97**, 2959; J. E. Szulejko, J. H. Bowie, I. Howe and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **34**, 99; M. M. Bursey, *Mass Spectrom. Rev.*, 1990, **9**, 555.

56 S. T. Graul and R. R. Squires, *J. Am. Chem. Soc.*, 1990, **112**, 2506.

57 K. M. Downard, R. N. Hayes and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1815.

58 G. N. Merrill, G. D. Dahlke and S. R. Kass, *J. Am. Chem. Soc.*, 1996, **118**, 4462.

59 H. Wincel, *Int. J. Mass Spectrom. Ion Processes*, 1998, **175**, 283, and references cited therein.

60 M. Frankowski, Z. Sun and A. M. Smith-Gicklhorn, *Phys. Chem. Chem. Phys.*, 2005, **7**, 797, and references cited therein.

61 M. B. Stringer, J. H. Bowie and J. L. Holmes, *J. Am. Chem. Soc.*, 1986, **108**, 3888.

62 J. S. Shannon, *Aust. J. Chem.*, 1962, **15**, 265.

63 S. J. Blanksby, D. Schröder, S. Dua, J. H. Bowie and H. Schwarz, *J. Am. Chem. Soc.*, 2000, **122**, 7105.

64 J. L. Holmes, *Org. Mass Spectrom.*, 1985, **20**, 169.

65 A. D. Becke, *J. Phys. Chem.*, 1993, **98**, 5648; P. J. Stevens, F. J. Devlin, C. F. Chablowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

66 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennuci, C. Pomelli, C. Amado, S. Clifford, J. Ochterski, G. A. Petrssen, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Latham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, revision A9*, Gaussian Inc., 1998.

67 M. W. Wong, *Chem. Phys. Lett.*, 1996, **256**, 391.

68 M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.*, 1994, **227**, 321.

69 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007; D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358.