ARTICLE

OBC
www.rsc.org/obc

Generation of transient neutrals in the gas phase from anionic precursors. Does energised CNCCO rearrange to NCCCO?

Andrew M. McAnoy, Suresh Dua† and John H. Bowie*
Department of Chemistry, The University of Adelaide, South Australia, 5005

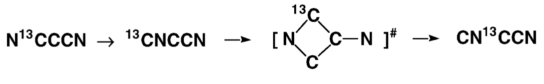
Received 8th March 2004, Accepted 30th April 2004
First published as an Advance Article on the web 24th May 2004

The stability and reactivity of the neutral species CNCCO generated by one electron oxidation of the anion [CNCCO]$^-$ have been investigated by a combination of theoretical calculations (carried out at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory) and tandem mass spectrometric experiments. Some of the neutrals formed in this way are stable for the microsecond duration of the experiment, but others are energised. The neutrals which are energised may either (i) dissociate [CNCCO $\longrightarrow$ CNC + CO (+92 kJ mol^{-1})], and/or (ii), undergo the isonitrile to nitrile rearrangement to yield NCCCO energised neutrals (barrier 133 kJ mol^{-1}, reaction exothermic by 105 kJ mol^{-1}). Some of these rearranged neutrals NCCCO have excess energies as high as 238 kJ mol^{-1} and will dissociate [NCCCO $\longrightarrow$ NCC + CO (+203 kJ mol^{-1})].

Introduction

Small unsaturated molecules are of much current interest to both chemists and astrophysicists. For example, the interstellar molecules C_3O, C_3S and C_3N have been studied both experimentally and theoretically.[1–4] Diheterocumulenes have also been studied, but none have, to date, been detected in interstellar or circumstellar dust clouds or in interstellar ice (*e.g.* the gas–ice interface of comets).[5,6] Carbon suboxide (OCCCO) is relatively stable,[7] NCCCO has been observed during neutralisation/reionisation experiments in mass spectrometers,[8,9] while transient NCCCN is available by photolysis or pyrolysis of dicyanodiazomethane,[10] or by neutralisation/reionisation of [NCCCN]$^-$,[11] and has been shown to be triplet by electron spin resonance spectroscopy.[12]

In previous studies we have shown that cumulenes and heterocumulenes formed with excess energies following vertical one-electron oxidation of anion precursors may undergo rearrangement of the cumulene backbone. Particular examples include the equilibration of the carbon atoms of (i) linear C_4, (a process which occurs *via* rearrangement through rhombic C_4[13]), and (ii) NCCCN.[10] The rearrangement of NCCCN is the most complex cumulene rearrangement that we have studied to date: theoretical calculations at the B3LYP/6-31G(d)//B3LYP/6-31+G(d) level of theory indicate that the $^3\Sigma_g^-$ ground state of NCCCN is 75 kJ mol^{-1} more stable than the $^1A_1$ state, and that rearrangement of the backbone requires the singlet NCCCN neutral to have an excess energy of $\geq$ 242 kJ mol^{-1}.[10] The rearrangement is outlined in Scheme 1 for the labelled molecule N^{13}CCCN. The structures in Scheme 1 show bond connectivities; they do not indicate bond multiplicities. The first step of the rearrangement involves a nitrile/isonitrile rearrangement. Cyclisation through a rhombic transition state followed by ring opening places the ^{13}C label in the centre of the molecule. The nitrile/isonitrile rearrangement is a key step in this rearrangement: typically, the energy difference between an isonitrile and a nitrile is 65 kJ mol^{-1} with the interconversion barrier (for RCN to RNC) about 190 kJ mol^{-1}.[14] In this case, molecular modelling indicates the difference between the two isomers to be 65 kJ mol^{-1} with the barrier 242 kJ mol^{-1}.[10]



Scheme 1

The corresponding neutral N^{13}CCCO can be formed by neutralisation/reionisation of [N^{13}CCCO]$^-$. There is no evidence of carbon scrambling of the nitrile to isonitrile rearrangement occurring when N^{13}CCCO is energised: instead, the neutral decomposes by loss of CO.[9] This is a general feature of cumulene oxides, when energised they lose CO rather than effect rearrangement of the cumulene system.[4,15] We have recently reported the formation of the related singlet cyanoketene (NCCHCO) by one electron oxidation of [NCCHCO]$^{-\bullet}$.[16] This species is stable under the conditions of the neutralisation/reionisation experiment: it neither rearranges to the less stable isonitrile [process endothermic (+118 kJ mol^{-1}) with a barrier of 246 kJ mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory] nor dissociates to CO and HCCN (dissociation energy 280 kJ mol^{-1}).[16]

Although it is not unreasonable that XC$_n$O systems should lose CO [because the negative heat of formation of CO (ΔH°_f (gas) = -110.5 kJ mol^{-1})[17] may reduce the endothermicity of the reaction sufficiently for the dissociation process to be observed under neutralisation/reionisation conditions], it is perhaps unusual that NCCCO should not undergo at least some rearrangement to the isonitrile isomer CNCCO. Although neither NCCCO nor CNCCO have been reported as interstellar molecules, they could, in principle, be useful intermediates in the formation of biomolecules, particularly in regions of interstellar ice. Nitriles constitute some of the most abundant of the 123 molecules so far identified in interstellar and circumstellar dust clouds.[5] Fifteen nitriles (or species which contain terminal CN groups) have been detected to date, whereas only five isonitriles have been reported; namely, HNC, CH$_2$NC, CH$_3$NC, MgNC and AlNC.[5]

In this paper we report the synthesis of [CNCCO]$^-$, and use this precursor to determine if we can make the neutral CNCCO, and if so, whether it rearranges to the more stable nitrile isomer.

Results and discussion

The experimental part of this study was always going to be a difficult undertaking. First, we had to ensure that the isonitrile precursor was introduced into the chemical ionisation source of the ZAB without undergoing thermal isomerisation to the isomeric nitrile. In addition there was the possibility that one (or more) of the CNCCO anion, neutral and/or cation may

---

† Land Operations Division, Defence, Science and Technology Organisation, P.O. Box 1500, Edinburgh, South Australia, 5111.

DOI: 10.1039/b403571m

Table 1 Geometries and energies of anions shown in Fig. 1

	^{1}**1**$^-$	^{1}**2**$^-$	^{1}**3**$^-$	TS1	TS2
State	$^1A'$	$^1A'$	$^1\Sigma$	—	$^1A'$
Relative energy (kJ mol^{-1})[a]	150	268	0	282	286
Dipole moment (Debye)	1.19	0.72	1.69	—	—
C_1N (Å)[b]	1.191	1.261	1.184	1.224	1.219
NC_2	1.327	1.506		1.483	1.929
C_1C_2		1.553	1.347	3.032	1.523
C_2C_3	1.260	1.261	1.251	1.278	1.274
C_3O	1.219	1.222	1.216	1.219	1.217
C_1NC_2 (°)	175.9	67.6		96.9	52.1
NC_1C_2		63.7	180.0		88.7
NC_2C_3	149.7	146.8		141.0	
$C_1C_2C_3$		164.5	180.0		149.6
C_2C_3O	171.6	178.0	180.0	167.1	168.7
$C_1NC_2C_3$	180.0	180.0		−9.6	
NC_2C_3O	180.0	180.0		−178.4	
$NC_1C_2C_3$			0.0		0.0
$C_1C_2C_3O$			0.0		180.0

[a] Energies are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to ^{1}**3**$^-$ (−243.700125 Hartrees). [b] B3LYP/6-31G(d) geometries.

(at least partially) rearrange to the isomeric NCCCO system. As a consequence, this discussion starts with a consideration of the theoretical aspects of the study, and concludes with the experimental data.

A Theoretical consideration of CNCCO and NCCCO systems

(i) The anions. The singlet form of $[CNCCO]^-$ lies 120 kJ mol^{-1} below the corresponding triplet at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory: as a consequence, the triplet anion is not considered further in this study. The reaction coordinate for the conversion of singlet $[CNCCO]^-$ to singlet $[NCCCO]^-$ is summarised in Fig. 1, while the geometries and energies of all minima and transition states shown in Fig. 1 are recorded in Table 1. The singlet $[CNCCO]^-$ anion is an unusual bent molecule (the NCC angle is 149.7°) lying 150 kJ mol^{-1} above linear $[NCCCO]^-$ on the singlet anion potential surface. If $[CNCCO]^-$ has an excess energy of $\geq$ 136 kJ mol^{-1} it may form a three membered cyclic intermediate which can ring open to form the isomer $[NCCCO]^-$ in a reaction exothermic by 150 kJ mol^{-1}. The conversion of $[NCCCO]^-$ to $[CNCCO]^-$ will not occur under the collisional conditions of a neutralisation/reionisation experiment, because the reverse activation energy of the process shown in Fig. 1 is too high (286 kJ mol^{-1}). The rearrangement of the isonitrile anion to the nitrile anion, although exothermic has a significant barrier of 136 kJ mol^{-1}. This barrier is not high enough to completely exclude the possibility of some isonitrile anions rearranging to the isomeric nitrile. On the other hand, the barrier is high enough to indicate that the anionic isonitrile to nitrile process is not facile. Another piece of information concerning the stability of singlet $[CNCCO]^-$ is that the decompositions of this species are high energy processes. The most favourable dissociation, $[CNCCO]^- \longrightarrow [CNC]^- + CO$, is endothermic by 296 kJ mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. The theoretical data suggest that singlet $[CNCCO]^-$ is a stable species, and that any isonitrile/nitrile rearrangement should be minor under the collisional conditions used for a neutralisation/reionisation experiment. We conclude that singlet $[CNCCO]^-$ is an appropriate precursor to be used in a one-electron vertical oxidation to form doublet CNCCO.

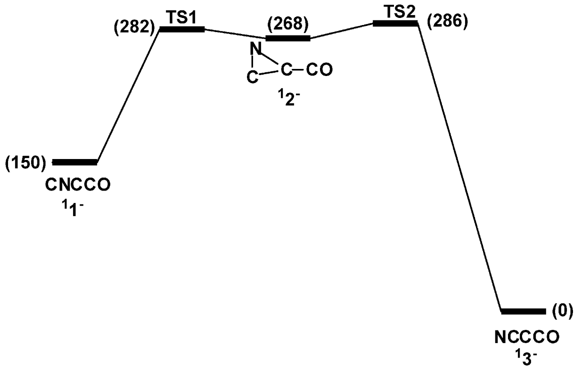


Fig. 1 The rearrangement of singlet $[CNCCO]^-$ to singlet $[NCCCO]^-$. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kJ mol^{-1}. For full details of geometries and energies see Table 1.

(ii) The neutrals. The data concerning the possible rearrangement of the doublet CNCCO to the isomer NCCCO are shown in Fig. 2 and Table 2. Doublet CNCCO has an adiabatic electron affinity of 3.01 eV, and is very similar in structure to the singlet anion $[CNCCO]^-$ (*cf.* data in Tables 1 and 2). In particular, both molecules are bent (the NCC angle in the anion is 149.7°; that of the neutral is 140.9°). Because these structures are so similar, the excess Franck–Condon energy of the neutral formed by vertical oxidation of the anion will be very small. This is another reason why $[CNCCO]^-$ should be, in principle, a good anionic precursor of neutral CNCCO.

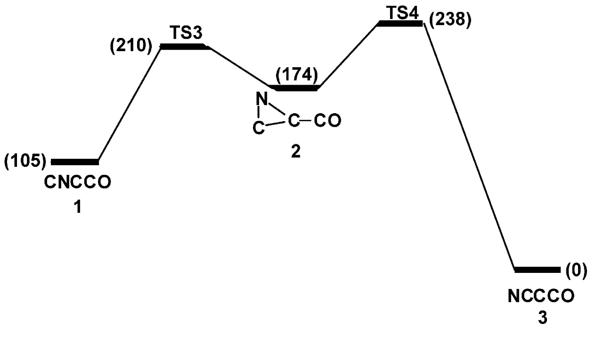


Fig. 2 The rearrangement of doublet CNCCO to doublet NCCCO. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kJ mol^{-1}. For full details of geometries and energies see Table 2.

The neutral rearrangement (Fig. 2) is similar to that already described for the singlet anion (Fig. 1). The differences lie in the relative energy differences which are smaller on the neutral potential surface. It has already been shown that gas-phase oxidation of $[NCCCO]^-$ to NCCCO does not result in rearrangement of NCCCO.[9] This experimental result is confirmed by the data shown in Fig. 2; in that the barrier (the

Table 2 Geometries and energies of neutrals shown in Fig. 2

	1	2	3	TS3	TS4
State	$^2A''$	$^2A''$	$^2\Pi$	$^2A''$	—
Relative energy (kJ mol^{-1})[a]	105	174	0	210	238
Dipole moment (Debye)	1.07	1.10	1.63	—	—
EA (eV)	3.01	2.50	3.47	—	—
IE (eV)	9.75	9.98	9.91	—	—
C_1N (Å)[b]	1.199	1.297	1.179	1.233	1.227
NC_2	1.305	1.400		1.394	1.710
C_1C_2		1.503	1.274	1.971	1.436
C_2C_3	1.302	1.300	1.331	1.299	1.292
C_3O	1.178	1.176	1.185	1.181	1.179
C_1NC_2 (°)	174.4	67.6		97.0	55.7
NC_1C_2		59.5	180.0		79.4
NC_2C_3	140.9	146.8		137.9	137.4
$C_1C_2C_3$		160.3	180.0		151.6
C_2C_3O	166.5	177.1	180.0	166.9	171.2
$C_1NC_2C_3$	180.0	180.0		180.0	138.6
NC_2C_3O	180.0	180.0		180.0	114.0
$NC_1C_2C_3$			180.0		−109.6
$C_1C_2C_3O$			180.0		−167.0

[a] Energies are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to **3** (−243.572571 Hartrees) [b] B3LYP/6-31G(d) geometries.

Table 3 Neutral dissociation energies[a]

Neutral processes		Dissociation energy (kJ mol^{-1})
NCCCO$^{\bullet}$	$\longrightarrow$ NCC$^{\bullet}$ + CO	203
	$\longrightarrow$ ^{3}CCO + CN$^{\bullet}$	453
	$\longrightarrow$ ^{1}CCCO + N$^{\bullet}$	418
	$\longrightarrow$ NCCC$^{\bullet}$ + O	615
CNCCO$^{\bullet}$	$\longrightarrow$ CNC$^{\bullet}$ + CO	92
	$\longrightarrow$ ^{3}CCO + CN$^{\bullet}$	348
	$\longrightarrow$ NCCO$^{\bullet}$ + C	435
	$\longrightarrow$ NCCC$^{\bullet}$ + O	615
^{1}NCCCN	$\longrightarrow$ NCC$^{\bullet}$ + CN$^{\bullet}$	422
	$\longrightarrow$ NCCC$^{\bullet}$ + N$^{\bullet}$	485

[a] Calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.

reverse activation barrier in Fig. 2) is high (239 kJ mol^{-1}). In contrast, CNCCO requires an excess energy of ≥ 133 kJ mol^{-1} to proceed through the cyclic intermediate, cleavage of which gives NCCCO in a reaction exothermic by 105 kJ mol^{-1}. This barrier is within the range we have observed before for rearrangements of cumulenes and heterocumulenes,[15] so the likelihood is that some of the initially formed neutral CNCCO molecules may have sufficient excess energy (produced by collision processes of the neutrals in the collision cell following the one-electron oxidation) to rearrange to more stable NCCCO molecules. The data in Fig. 2 show that if the neutral rearrangement occurs, the neutral NCCCO products of this process may have excess energies as high as 238 kJ mol^{-1}. The dissociation energies of neutral CNCCO and NCCCO are listed in Table 3. If neutrals NCCCO are produced by rearrangement, they should have sufficient excess energy to dissociate to NCC and CO (dissociation energy 203 kJ mol^{-1}). It is also of interest to compare the excess energy required to rearrange CNCCO to NCCCO (133 kJ mol^{-1}, Fig. 2) with that required to effect dissociation of CNCCO. The lowest energy dissociation of CNCCO is that which forms CNC and CO (+92 kJ mol^{-1}, see Table 3). These data, when considered together, indicate that (i) when CNCCO is energised, it is as likely (perhaps more likely) to dissociate to CNC and CO than rearrange to NCCCO, and (ii) if there is rearrangement to NCCCO, the majority of these neutrals will be energised and dissociate to give NCC and CO.

(iii) The cations. The situation concerning the cation surfaces is complex, because the ground state triplet [CNCCO]$^+$ lies only 7 kJ mol^{-1} below singlet [CNCCO]$^+$. Although the energies of these species are similar, their geometries are quite different. The ground state triplet is linear (Table 4), whereas the singlet cation is bent [angle NCC is 125.9° (Table 5): *cf.* anion, 149.7° (Table 1), neutral, 140.9° (Table 2)]. Since the singlet and triplet cations are so close in energy, both will be accessible by Franck–Condon oxidation of the neutral. Thus we need to consider the potential surfaces of both the triplet and singlet cations. The reaction coordinates of triplet and singlet rearrangements are summarised in Figs. 3 and 4 respectively, with full details of geometries and energies listed in Tables 4 and 5. In this treatment we have treated both singlet and triplet cations separately, and have not considered the possibility of spin crossing.

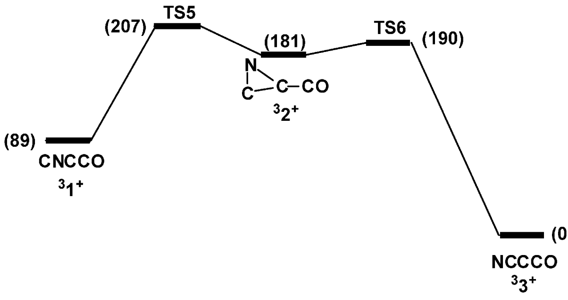


Fig. 3 The rearrangement of triplet [CNCCO]$^+$ to triplet [NCCCO]$^+$. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kJ mol^{-1}. For full details of geometries and energies see Table 4.

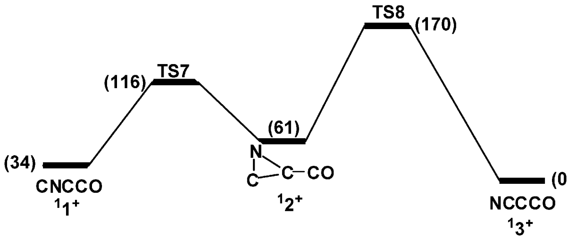


Fig. 4 The rearrangement of singlet [CNCCO]$^+$ to singlet [NCCCO]$^+$. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kJ mol^{-1}. For full details of geometries and energies see Table 5.

The reaction coordinate for the rearrangement of triplet [CNCCO]$^+$ to triplet [NCCCO]$^+$ is shown in Fig. 3, with full details of geometries and energies given in Table 4. The mech-

Table 4 Geometries and energies of triplet cations shown in Fig. 3

	^{3}**1**$^+$	^{3}**2**$^+$	^{3}**3**$^+$	TS5	TS6
State	$^3\Sigma$	$^3A''$	$^3A'$	$^3A''$	$^3A''$
Relative energy (kJ mol^{-1})[a]	89	181	0	207	190
Dipole moment (Debye)	0.01	1.47	1.02	—	—
C_1N (Å)[b]	1.232	1.255	1.211	1.250	1.225
NC_2	1.250	1.504		1.355	1.802
C_1C_2		1.400	1.300	1.674	1.385
C_2C_3	1.306	1.333	1.319	1.324	1.318
C_3O	1.156	1.148	1.146	1.152	1.152
C_1NC_2 (°)	180.0	60.1		79.8	50.1
NC_1C_2		68.8	180.0	52.9	87.1
NC_2C_3	180.0	141.7		155.9	131.2
$C_1C_2C_3$		167.2	180.0	156.8	174.0
C_2C_3O	180.0	179.3	180.0	176.2	177.2
$C_1NC_2C_3$	0.0	180.0		180.0	
NC_2C_3O	0.0	180.0		180.0	
$NC_1C_2C_3$			0.0		0.0
$C_1C_2C_3O$			0.0		180.0

[a] Energies are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to ^{3}**3**$^+$ (−243.208221 Hartrees). [b] B3LYP/6-31G(d) geometries.

Table 5 Geometries and energies$^+$ of singlet cations shown in Fig. 4.

	^{1}**1**$^+$	^{1}**2**$^+$	^{1}**3**$^+$	TS7	TS8
State	$^1A'$	$^1A'$	$^1A'$	$^1A'$	—
Relative energy (kJ mol^{-1})[a]	34	61	0	116	170
Dipole moment (Debye)	0.23	1.36	0.90	—	—
C_1N (Å)[b]	1.233	1.390	1.197	1.268	1.235
NC_2	1.271	1.309	1.326	1.334	1.681
C_1C_2		1.454		1.944	1.379
C_2C_3	1.423	1.385	1.354	1.420	1.354
C_3O	1.139	1.133	1.144	1.140	1.146
C_1NC_2 (°)	168.7	65.1		96.6	53.9
NC_1C_2		54.7	175.4	43.0	79.8
NC_2C_3	125.9	141.0		125.1	144.7
$C_1C_2C_3$		158.9	139.5		141.3
C_2C_3O	157.0	174.7	168.9	157.7	168.2
$C_1NC_2C_3$	180.0	180.0		180.0	
NC_2C_3O	180.0	180.0		180.0	
$NC_1C_2C_3$			180.0		−127.8
$C_1C_2C_3O$			180.0		−177.6

[a] Energies are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to ^{1}3$^+$ (−243.184614 Hartrees). [b] B3LYP/6-31G(d) geometries.

Table 6 Cation dissociation energies[a]

Singlet cation processes		Dissociation energy (kJ mol^{-1})	Triplet cation processes		Dissociation energy (kJ mol^{-1})
$^1NCCCO^+$	$\longrightarrow {}^1NCC^+ + CO$	199	$^3NCCCO^+$	$\longrightarrow {}^3NCC^+ + CO$	420
	$\longrightarrow CCO^+ + CN^\bullet$	461		$\longrightarrow CCO^+ + CN^\bullet$	523
	$\longrightarrow CCCO^+ + N^\bullet$	435		$\longrightarrow CCCO^+ + N^\bullet$	497
	$\longrightarrow {}^3NCCC^+ + O$	700		$\longrightarrow {}^1NCCC^+ + O$	810
$^1CNCCO^+$	$\longrightarrow {}^1CNC^+ + CO$	65	$^3CNCCO^+$	$\longrightarrow {}^3CNC^+ + CO$	320
	$\longrightarrow CCO^+ + CN^\bullet$	427		$\longrightarrow CCO^+ + CN^\bullet$	434
	$\longrightarrow {}^3NCCO^+ + C$	691		$\longrightarrow {}^1NCCO^+ + C$	336
	$\longrightarrow {}^3NCCC^+ + O$	722		$\longrightarrow {}^1NCCC^+ + O$	751

[a] Calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.

anism of the rearrangement sequence is similar to those of the anion and neutral (considered earlier). The reaction is exothermic by 89 kJ mol^{-1}, with the triplet [CNCCO]$^+$ species requiring an excess energy of ≥ 118 kJ mol^{-1} to effect rearrangement to [NCCCO]$^+$. This barrier is certainly within the range of those cation rearrangements we have observed previously in heterocumulene $^-$NR$^+$ spectra.[15] The data in Table 6 show that all dissociations of triplet [CNCCO]$^+$ are high energy processes and will not compete with the rearrangement shown in Fig. 3. The product of the rearrangement, triplet [NCCCO]$^+$ is formed with a maximum excess energy of 207 kJ mol^{-1}; this is not sufficient to cause any of the dissociations of the triplet [NCCCO]$^+$ listed in Table 6.

The data in Fig. 4 and Table 5 suggest that singlet [CNCCO]$^+$ might also undergo rearrangement. The rearrangement is again exothermic (−34 kJ mol^{-1}), but with a barrier of 136 kJ mol^{-1} (compare with the barrier of 118 kJ mol^{-1} for the corresponding triplet rearrangement). However, the rearrangement is unlikely to occur, because if singlet [CNCCO]$^+$ has an excess energy of 136 kJ mol^{-1}, it would be expected to undergo dissociation to ^{1}[CNC]$^+$ and CO (dissociation energy +65 kJ mol^{-1}; see Table 6), rather than rearrange to singlet [NCCCO]$^+$.

To summarise the conclusions of the theoretical investigation:

(i) There should be little rearrangement of singlet [CNCCO]$^-$ to singlet [NCCCO]$^-$; singlet [CNCCO]$^-$ should therefore be a good precursor for doublet CNCCO,

(ii) Doublet CNCCO occupies a minimum on the neutral C_3NO potential surface. If energised, CNCCO may undergo two competing processes. It may dissociate to CNC and CO, or rearrange to NCCCO, which has sufficient excess energy to cause dissociation to NCC and CO. This suggests that neutralisation of [CNCCO]$^-$ will produce CNCCO and the decomposition products CNC, NCC and CO, together with a lesser amount of stable NCCCO.

(iii) One electron vertical oxidation of CNCCO will form both singlet and triplet [CNCCO]$^+$. If the triplet ground state has an excess energy of ≥ 118 kJ mol^{-1}, it will rearrange to triplet [NCCCO]$^+$. Rearrangement of singlet [CNCCO]$^+$ to singlet [NCCCO]$^+$ requires the isonitrile to have an excess energy of ≥ 136 kJ mol^{-1}. This rearrangement is unlikely to occur because the dissociation energy of the process ^{1}[CNCCO]$^+$ ⟶ ^{1}[CNC]$^+$ + CO is only 65 kJ mol^{-1}. Thus both the $^-$CR$^+$ and $^-$NR$^+$ spectra of [CNCCO]$^-$ should show a parent peak due to both rearranged [NCCCO]$^+$ and unrearranged [CNCCO]$^+$ together with fragment cations from (a) both parent cations, and (b) by ionisation of fragment neutrals.

B The experimental evidence – the $^-$CR$^+$ and $^-$NR$^+$ spectra of [CNCCO]

The theoretical data suggest that [CNCCO]$^-$ is a stable species and if there is any rearrangement to the stable isomer [NCCCO]$^-$, it will be a minor process. The collision induced mass spectrum (MS/MS) of [NCCCO]$^-$ has been reported:[9] it shows small losses of C, N, O and C_2 with the base peak at *m*/*z* 38 (loss of CO). The MS/MS of [CNCCO]$^-$ is different, in that it shows only a parent anion together with minor loss of CO. The peak width at half height of the peaks formed by loss of CO in the two spectra are different by 6.4 V {[CNCCO]$^-$ (77.4 ± 0.5 V); [NCCCO]$^-$ (71.0 ± 0.5 V)}. The differences in the MS/MS data, considered together with earlier theoretical data, suggest that [CNCCO]$^-$ retains its structure when energised, but do not exclude the possibility of minor rearrangement to [NCCCO]$^-$.

The $^-$CR$^+$ and $^-$NR$^+$ spectra of [CNCCO]$^-$ are recorded in Fig. 5, and these should be compared with the corresponding spectra of [NCCCO]$^-$, shown in Fig. 6. The two $^-$CR$^+$ spectra are similar, but there are two significant differences. These are the peaks at *m*/*z* 54 (loss of C) and 12 (formation of $C^{+\cdot}$) in the $^-$CR$^+$ spectrum of [CNCCO]$^-$; these peaks are absent in the $^-$CR$^+$ spectrum of [NCCCO]$^-$. The presence of these two peaks indicate that some [CNCCO]$^+$ cations survive the two-electron oxidation of [CNCCO]$^-$. The $^-$NR$^+$ and $^-$CR$^+$ spectra of [CNCCO]$^-$ are qualitatively similar; the main difference is that the peak corresponding to loss of CO is larger in the $^-$NR$^+$ spectrum. A comparison of the two $^-$NR$^+$ spectra indicates that the loss of CO is more intense in that of [CNCCO]$^-$.

The experimental data are largely in agreement with the more detailed theoretical study considered earlier. The loss of C and the formation of $C^{+\bullet}$ in the $^-$NR$^+$ spectrum of [CNCCO]$^-$ confirms that some of the CNCCO neutrals survive neutralisation of the anion, *i.e.* within the experimental timeframe of microseconds. The large peak in the $^-$NR$^+$ spectrum of [CNCCO]$^-$ due to the loss of CO can be attributed to either (i) decomposition of CNCCO {CNCCO ⟶ CNC + CO (+92 kJ mol^{-1}, Table 3)} followed by ionisation of CNC, and/or (ii) decomposition of singlet [CNCCO]$^+$ {^{1}[CNCCO]$^+$ ⟶ ^{1}[CNC]$^+$ + CO (+65 kJ mol^{-1}, Table 6)}. These figures should be compared with the higher endothermicity of the corresponding dissociation processes of triplet [CNCCO]$^+$, neutral NCCCO and both singlet and triplet [NCCCO]$^+$ (Tables 3 and 6).

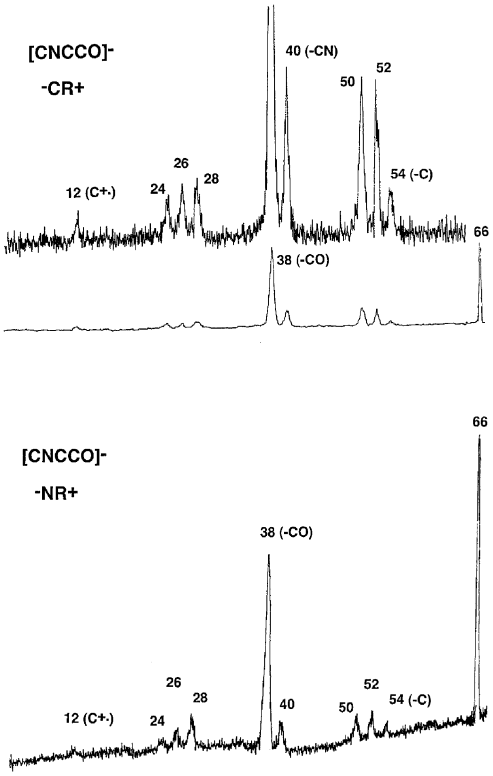


Fig. 5 $^-$CR$^+$, and $^-$NR$^+$ mass spectra of [CNCCO]$^-$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental section.

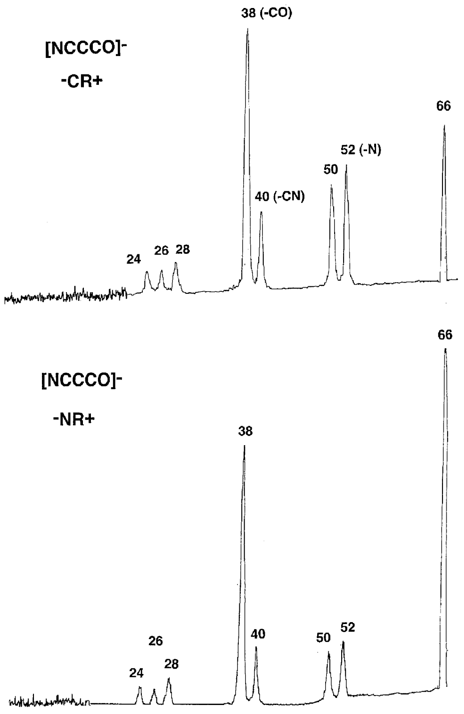


Fig. 6 $^-$CR$^+$, and $^-$NR$^+$ mass spectra of [NCCCO]$^-$.[9] VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental section.

In conclusion, a combination of data provided by both experimental and theoretical studies, indicate:-

(a) Precursor anion [CNCCO]$^-$ is a stable species.

(b) One electron oxidation of [CNCCO]$^-$ produces some neutrals CNCCO that are stable for the microsecond timeframe of the NR process.

(c) One electron oxidation of [CNCCO]$^-$ also gives energised CNCCO neutrals. Some of these may (i) dissociate to give CNC and CO, and/or (ii) rearrange to NCCCO, which is energised and may decompose to NCC and CO.

(d) One-electron oxidation of CNCCO and two-electron oxidation of $[CNCCO]^-$ both yield a mixture of decomposing and non-decomposing cations $[CNCCO]^+$ and $[NCCCO]^+$.

Experimental

A Mass spectrometric experiments

All experiments were performed with a VG ZAB 2HF two-sector mass spectrometer of BE configuration (B stands for magnetic and E for electric sector), which has been described previously.[18] In summary, the precursor anion $[CNCCO]^-$ was prepared in the chemical ionisation (CI) source of the mass spectrometer as follows. The neutral $CNCH_2CO_2Et$ was introduced *via* the direct probe in which the 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 chemical ionisation source were heated to 50 °C, conditions under which the isonitrile is stable. The substrate was allowed to react with HO^- in the ion source (from H_2O, measured pressure was 10^{-5} Torr in the source housing; estimated pressure in the chemical ionisation source 10^{-1} Torr) by the standard processes (a) $CNCH_2CO_2Et + HO^- \longrightarrow [CN^-CHCO_2Et] + H_2O$, and (b) $[CN^-CHCO_2Et] \longrightarrow [(CNCHCO)^-OEt] \longrightarrow [CNCCO]^- + EtOH$.[9] Anions were accelerated to 7 keV translational energy and mass selected by means of the magnet. For collisional activation experiments, the ions were collided in the field free regions between B and E with helium at 80% transmission (T) of the incident beam; these conditions approximate single-collision conditions.[19]

In neutralisation/reionisation experiments ($-NR^+$),[20] the radical ions were neutralised by high-energy collisions with molecular oxygen (80% T) in the first of the 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 by collision with oxygen (80% T).

The resulting mass spectra were recorded by scanning E. Charge reversal mass spectra of the anions to cations ($^-CR^+$)[21] were obtained by colliding the ion beam with oxygen (80% T) in the field free region preceding E. Under these conditions, the CR process can be treated as a vertical, two-electron oxidation occurring in a single step at a time scale of a few femtoseconds, although some species may undergo multiple collisions.

B Precursor molecules

The precursor $CNCH_2CO_2Et$ is commercially available and was used without purification.

C Theoretical methods

Geometry optimizations were carried out with the Becke 3LYP method[22] using a modest 6-31G(d) basis within the GAUSSIAN 98 suite of programs.[23] Stationary points were characterised as either minima (no imaginary frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were then scaled[24] by 0.9804 and used as a zero-point correction for the electronic energies calculated at this and higher levels of theory. More accurate energies for the B3LYP geometries were determined using the CCSD(T) method[25] together with the Dunning aug-cc-pVDZ basis set.[26]

Calculations were carried out on the alpha server supercomputer (APAC) at the Australian National University (Canberra).

Acknowledgements

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

References

1 R. D. Brown, F. W. Eastwood, P. S. Elmes and P. J. Godfrey, *J. Am. Chem. Soc.*, 1983, **105**, 6496.
2 R. D. Brown, D. E. Pullin, E. H. B. Rice and M. Rodler, *J. Am. Chem. Soc.*, 1985, **107**, 7877.
3 Y. Hiratam, Y. Ohshima and Y. Endo, *J. Chem. Phys.*, 1994, **101**, 7342; Y. Kasai, Y. Sumiyoshi and K. Kawaguchi, *Astrophys. J.*, 1997, **477**, L65.
4 K. Tran, A. M. McAnoy and J. H. Bowie, *Org. Biomol. Chem.*, 2004, 999.
5 For a list of the 123 molecules detected so far see: H. A. Wootten, http://www.cv.nrao.edu/~allmols.html.
6 N. Boudin, W. A. Schutte and J. M. Greenberg, *Astron. Astrophys.*, 1998, **331**, 749; H. Cottin, M. C. Cazeau and F. Raulin, *Planet. Space Sci.*, 1999, **47**, 1141 and references cited therein.
7 T. Kappe and E. Zeigler, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 491.
8 C. A. Muedas, D. Sülze and H. Schwarz, *Int. J. Mass Spectrom. Ion Processes*, 1992, **113**, R17.
9 S. Dua and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 2001, 652.
10 A. G. Anastassiou and H. E. Simmons, *J. Am. Chem. Soc.*, 1965, **87**, 3177; A. G. Anastassiou, *J. Am. Chem. Soc.*, 1967, **89**, 3177.
11 S. J. Blanksby, S. Dua, J. H. Bowie, D. Schröder and H. Schwarz, *J. Phys. Chem. A*, 2000, **104**, 11248.
12 E. Wasserman, L. Barash and W. A. Yager, *J. Am. Chem. Soc.*, 1965, **87**, 2076.
13 S. J. Blanksby, D. Schrõder, S. Dua, J. H. Bowie and H. Schwarz, *J. Am. Chem. Soc.*, 2000, **122**, 7105.
14 G. Kohlmaier and B. S. Rabinovich, *J. Phys. Chem.*, 1959, **63**, 1793.
15 S. Dua, S. J. Blanksby, S. Peppe, A. M. McAnoy and J. H. Bowie, *Curr. Org. Chem.*, 2003, **7**, 1.
16 A. M. McAnoy, S. Dua and J. H. Bowie, *J. Phys. Chem. A.*, 2004, **108**, 3994.
17 NIST JANAF Thermochemical Tables, *J. Phys. Chem. Ref. Data*, Monograph 9, 4th Edn., American Chemical Society, 1998.
18 M. B. Stringer, J. H. Bowie and J. L. Holmes, *J. Am. Chem. Soc.*, 1986, **108**, 3888.
19 J. L. Holmes, *Org. Mass Spectrom.*, 1985, **20**, 169.
20 A. W. McMahon, S. K. Chowdhury and A. G. Harrison, *Org. Mass Spectrom.*, 1989, **24**, 620; N. Goldberg and H. Schwarz, *Acc. Chem. Res.*, 1994, **27**, 347.
21 J. H. Bowie and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **20**, 169; 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.
22 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.
23 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98 (Revision A.9), Gaussian, Inc., Pittsburgh, PA, 1998.
24 M. W. Wong, *Chem. Phys. Lett.*, 1996, **256**, 391.
25 M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.*, 1994, **227**, 321 and references cited therein.
26 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007; D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358.