A novel anion rearrangement. The conversion of $[CC(O)(CN)]^-$ to $[NCCCO]^-$ in the gas phase: a joint experimental and theoretical study

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Suresh Dua and John H. Bowie

Department of Chemistry, The University of Adelaide, South Australia, 5005

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The neutral radical $N^{13}CCCO$ has been made by charge stripping of anion $[N^{13}CCCO]^-$ in a collision cell of a ZAB 2HF mass spectrometer. The precursor anion is formed in the ion source of the mass spectrometer by the loss of the elements of MeOH from the anion $N^{13}C{-}^{-}CHCO_2Me$. Neutral $N^{13}CCCO$ can, in turn, be charge stripped to the corresponding cation $[N^{13}CCCO]^+$ which then decomposes by competitive losses of CO and $N^{13}C^•$. No losses of ^{13}CO or $NC^•$ are observed in this spectrum: thus, the neutral $N^{13}CCCO$ does not scramble the carbons in the carbon chain during the lifetime (*ca.* 10^{-6} s) of the neutral. An attempt to form the neutral radical CC(O)(CN) (which is isomeric with NCCCO) from the precursor anion $[CC(O)(CN)]^-$ was unsuccessful, since on formation, $[CC(O)(CN)]^-$ undergoes facile rearrangement to the more stable $[NCCCO]^-$. A theoretical investigation at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory indicates that (i) there are singlet and triplet forms of $[CC(O)CN]^-$ which are only 7 kJ mol^{-1} different in energy, and (ii) both of these ions undergo facile rearrangement to form the respective singlet and triplet forms of $[NCCCO]^-$ in strongly exothermic reactions.

Introduction

We have recently reported the syntheses of a number of stellar and potential stellar molecules in collision cells of a mass spectrometer, including cumulenes[1,2] and heterocumulenes.[1] These molecules are normally produced by charge stripping of precursor anions of known bond connectivity. Heterocumulenes studied include C_3O,[3] C_5O isomers,[4] C_7O,[5] C_nO_n (n = 2–6),[6,7] NCN,[8] and NC_3N.[8]

One of the interesting features of some cumulenes is that, when energised, they may undergo reorganisation of the carbon chain. For example, linear C_4 rearranges to the more stable rhombus C_4.[2] In the case of energised heterocumulene neutrals, rearrangement of both the heteroatom and the carbon chain may occur: for example C_2COC_2 rearranges to the more stable C_4CO,[4] while NCCCN rearranges to CNCCN and also scrambles the carbons.[8] This suggests that when molecules of this type are formed in either interstellar dust clouds or circumstellar envelopes, there is the potential for rearrangement of such molecules to other isomers.[1,9]

In the current study we extend our work on heterocumulenes to study the formation and properties of NCCCO (an oxygen analogue of NCCCN) and to investigate the synthesis of the isomer CC(O)(CN). Schwarz and co-workers have made NCCCO by charge stripping of the $NC{-}^{-}CHCO_2Me$ anion,[10a] while Wentrup has made the hydrogen analogue HNCCCO from a heterocyclic precursor.[10b] Our aim is to make the two neutral isomers NCCCO and CC(O)(CN) from anionic precursors, and to ascertain (i) whether NCCCO rearranges to the isonitrile and scrambles the carbons (like NCCCN[8]), and (ii) whether CC(O)(CN) rearranges to the more thermodynamically stable NCCCO.

Results and discussion

The formation of NCCCO and the labelled derivative $N^{13}CCCO$

We have prepared anion $[NCCCO]^-$ by the method adopted by Schwarz *et al.*[10a] as shown in eqn. (1). The collisional activation

$$NCCH_2CO_2Me \xrightarrow{HO^-} NC{-}^{-}CHCO_2Me \longrightarrow$$
$$[(NC{-}CH{=}C{=}O)\ ^{-}OMe] \xrightarrow{-MeOH} [NCCCO]^- \quad (1)$$

(CA), charge reversal (CR) and neutralisation reionisation ($^-NR^+$) spectra, are similar to those reported earlier by Schwarz *et al.*,[10a] and are recorded in Table 1. We have reported

Table 1 CA, CR and $^-NR^+$ mass spectra of $[NCCCO]^-$, $[N^{13}CCCO]^-$ and $[CC(O)(CN)]^-$

Anion	Mode	Spectrum [*m*/*z* (relative abundance)]
$[NCCCO]^-$	CA	66, 54(<1),[a] 52(4), 50(7), 40(8), 38(100), 26(2)
	CR	66(100), 52(7), 50(7), 40(4), 38(18), 28(1), 26(1), 24(1), 12(0.4)
	$^-NR^+$	66(100), 52(6), 50(5), 40(5), 38(30), 28(2), 26(1), 24(2)
$[N^{13}CCCO]^-$	CA[b]	67, 39(100)
	CR	See Fig. 1
	$^-NR^+$	See Fig. 1
$[CC(O)(CN)]^-$	CA	See Fig. 2
	CR	66(100), 52(4), 50(3), 40(4), 38(16), 28(1), 26(1), 24(1), 12(0.3)
	$^-NR^+$	66(100), 52(10), 50(7), 40(6), 38(25), 28(1), 26(1), 24(1)

[a] If this peak is present at all, it is lost in baseline noise. [b] This is a weak spectrum: there are other peaks but they are obscured by baseline noise.

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that neutral NCCCN undergoes both the nitrile–isonitrile rearrangement and carbon scrambling *via* three-membered ring formation and ring opening mechanisms.[8] Does the analogue NCCCO undergo similar rearrangements? In order to answer this question we have synthesised the labelled precursor $N^{13}CCH_2CO_2Me$, deprotonated it to give the anion $N^{13}C{-}^{-}CHCO_2Me$, which decomposes to form the required labelled species $[N^{13}CCCO]^-$.

The CA spectrum of $[N^{13}CCCO]^-$ is recorded in Table 1, while the corresponding CR and $^-NR^+$ mass spectra are recorded in Fig. 1. There is no indication of carbon scrambling occurring for the anion, neutral molecule or the decomposing cation. As an illustration, both the CR and $^-NR^+$ spectra show specific loss of ^{13}CN and ^{12}CO: no losses of ^{12}CN and/or ^{13}CO are noted. These data show that there is no scrambling of the C chain which accompanies or precedes these losses, in contrast with the scrambling which occurs for the analogue NCCCN. In addition, there is no evidence to suggest that the nitrile to isonitrile rearrangement is occurring, because there is no loss of C in the CR or $^-NR^+$ spectra of $[NCCCO]^-$ (Table 1), or loss of ^{13}C in the corresponding spectra of $[N^{13}CCCO]^-$ (Fig. 1).

The structures and relative energies of anions, neutral species and cations corresponding to NCCCO have been calculated at the respective B3LYP/6-31G(d) and B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) levels of theory: these data, together with dipole moments of all species, are summarised in Table 2. All states are best represented as linear heterocumulene structures. The ground state anion is a singlet, while the ground state cation is a triplet.

A reviewer has questioned the applicability of the level of calculation that we have used in this study. We answer those queries here. Firstly, the reviewer suggests that geometries of the anions would be better calculated at the 6-31+G(d) level. The calculated geometries of singlet $[NCCCO]^-$ at the 6-31G(d) and 6-31+G(d) levels are listed in Table 2: they are essentially the same. Secondly, the reviewer has stated that B3LYP methods do not give good energies for carbenoid cumulenes. It is true that problems have been highlighted regarding the use of the B3LYP method for the accurate prediction of energies for carbon clusters,[11] although the method continues to be used with success.[12,13] To overcome any potential problem of this nature, we have determined more accurate energies for the B3LYP/6-31G(d) geometries using the Dunning aug-cc-pVDZ basis set.[14,15] The CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) approach predicts electron affinities close to experimental values for the following systems, *viz.* C_3H (calculated 1.79, experimental 1.86)[16] and C_4 (calculated 3.65, experimental 3.88 eV).[2] In addition, similar B3LYP calculations for C_5H isomers[17] show little deviation from those determined for the same systems using more rigorous coupled-cluster approaches.[18] We have not used the CCSD(T) level of theory for the five atom systems C_3NO. However the use of the CCSD(T) level of theory to calculate energy splitting between the singlet and triplet forms of $[NCCCO]^-$ shows a value very close to that calculated at the lower level, *viz.* B3LYP/aug-cc-pVDZ//B3LYP/

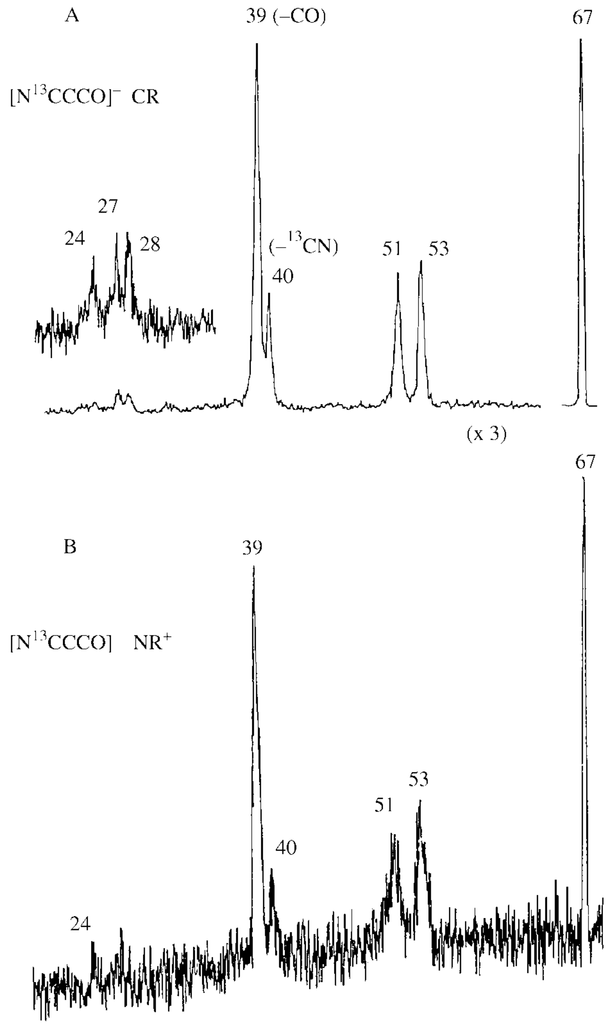


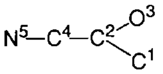
Fig. 1 (A) Charge reversal (CR) and (B) neutralisation reionisation ($^-NR^+$) mass spectra (MS/MS) of $[N^{13}CCCO]^-$. VG ZAB 2HF mass spectrometer. For experimental conditions see the Experimental section.

Table 2 Theoretical calculations for anions, neutral and cations of linear NC_3O

	Anion (singlet)	Anion (triplet)	Neutral	Cation (singlet)	Cation (triplet)
State	$^1\Sigma$		$^2\Pi$	$^1\Pi$	$^3\Sigma$
Symmetry	$C_{\infty v}$	C_1	$C_{\infty v}$	$C_{\infty v}$	$C_{\infty v}$
Energy/hartree[a]	−244.32080	−244.22669	−244.19095	−243.78073	−243.81761
Relative energy/kJ mol^{-1}	0.0	247	341	1418	1332
Dipole moment/debye	1.69	1.37	1.63	0.70	1.02
C^1C^2/Å[b]	1.251	1.437	1.274	1.315	1.319
C^2O^3/Å	1.216	1.226	1.179	1.150	1.146
C^1C^4/Å	1.347	1.361	1.331	1.305	1.300
C^4N^5/Å	1.184	1.196	1.185	1.202	1.211
$C^1C^2O^3$/°	180.0	127.2	180.0	180.0	180.0
$C^2C^1C^4$/°	180.0	125.4	180.0	180.0	180.0
$C^1C^4N^5$/°	180.0	172.4	180.0	180.0	180.0
$C^4C^1C^2O^3$/°	0.0	146.2	0.0	0.0	0.0
$C^2C^1C^4N^5$/°	0.0	−173.8	0.0	0.0	0.0

[a] B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory including zero-point vibrational energy [calculated from vibrational frequencies at B3LYP/6-31G(d) level of theory and scaled by 0.9804[34]]. [b] B3LYP/6-31G(d) level of theory. The calculated geometric parameters calculated for the singlet anion, using the B3LYP/6-31+G(d) level of theory, are: C^1C^2 (1.252), C^2O^3 (1.216), C^1C^4 (1.348), C^4N^5 (1.185 Å), $C^1C^2O^3$ (180.0), $C^2C^1C^4$ (180.0), $C^1C^4N^5$ (180.0), $C^4C^1C^2O^3$ (0.0) and $C^2C^1C^4N^5$ (0.0°) [compare with the B3LYP/6-31G(d) parameters shown in column 2].

Table 3 Theoretical calculations for anions, neutral and cations of branched NC_3O



	Anion (singlet)	Anion (triplet)	Neutral	Cation (singlet)	Cation (triplet)
State	$^1A'$	$^3A''$	$^2A''$	$^1A'$	$^3A''$
Symmetry	C_s	C_s	C_s	C_s	C_s
Energy/hartree[a]	−244.1929774	−244.1902396	−244.0895764	−243.7155931	−243.6564492
Relative energy/kJ mol^{-1}	0	7.1	272	1254	1409
Dipole moment/debye	1.89	2.00	0.57	1.58	2.44
C^1C^2/Å[b]	1.344	1.424	1.371	1.476	1.510
C^2O^3/Å	1.324	1.270	1.364	1.296	1.205
C^2C^4/Å	1.444	1.498	1.386	1.373	1.431
C^4N^5/Å	1.170	1.170	1.168	1.173	1.172
C^1O^3/Å			1.506	1.415	
$C^1C^2O^3$/°	104.8	129.7	66.8	61.0	128.5
$C^1C^2C^4$/°	128.9	113.7	159.6	163.8	96.0
$C^4C^2O^3$/°	126.3	116.6	133.6	135.3	135.1
$C^2C^4N^5$/°	178.3	178.1	178.4	176.6	170.7

[a] B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory including zero-point vibrational energy [calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804[34]]. [b] B3LYP/6-31G(d) level of theory.

6-31G(d) [247 kJ mol^{-1} (Table 2)] and CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) [243 kJ mol^{-1}]. Thus the level of calculation used for this study affords acceptable geometries and energies at reasonable computational cost.

Attemped formation of the neutral CC(O)(CN)

We next wished to make an isomer of NCCCO in order to see whether the isomer would rearrange to the more stable NCCCO under the reaction conditions. Apart from the rearrangement of NCCCN[8] we have also shown that neutral CCC(O)CC rearranges to CCCCCO (which is more stable than CCC(O)CC by 377 kJ mol^{-1}) over a barrier of only 36 kJ mol^{-1}.[4] The isomer we have chosen to study in this case is CC(O)(CN). The geometries and energies of the anions, neutral and cations of CC(O)(CN) neutrals have been calculated respectively at the B3LYP/6-31G(d) and B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory, and are summarised in Table 3. Comparison of data in Tables 2 and 3 shows that neutral radical CC(O)(CN) is 266 kJ mol^{-1} less stable than NCCCO at the level of theory used. The data in Table 3 also show that the geometry of the ground state singlet form of $[CC(O)(CN)]^-$ is different from the structure of the ground state neutral. The distance between C^1 and O in the neutral is 1.506 Å and angle C^1C^2O is 66.8°. Thus in the neutral, C^1, C^2 and O encompass a distorted three-membered ring. This three-membered ring structure is not a feature of the anion where angle C^1C^2O is 104.8° (Table 3). Because of the difference in structure between the anion and the neutral, vertical Franck–Condon charge stripping of the anion will produce an energised neutral: perhaps this excess energy will be sufficient to effect rearrangement to the more stable neutral radical NCCCO (*cf.* ref. 8).

The negative ion precursor of CC(O)(CN) is accessible *via* the reaction sequence shown in eqn. (2). This process involves

$$CH_2{=}C(OMe)(CN) + O^{-\bullet} \xrightarrow{-H_2O} [C{=}C(OMe)(CN)]^{-\bullet} \longrightarrow [CC(O)CN]^- + Me^\bullet \quad (2)$$

reaction of $CH_2{=}C(OMe)(CN)$ with the mono-oxygen radical anion, a reaction[19] which yields $[C{=}C(OMe)(CN)]^{-\bullet}$ which then decomposes by loss of a methyl radical. The expected peak at *m*/*z* 65 is the major fragment ion observed when $CH_2{=}C(OMe)(CN)$ is allowed to react with $O^{-\bullet}$ in the chemical ionisation source of the ZAB mass spectrometer.

The CA mass spectrum of *m*/*z* 65 is shown in Fig. 2. This spectrum is very similar to that of $[NCCCO]^-$ (Table 1). The main fragment ion in Fig. 2 is produced by loss of CO from the parent anion, a process not possible from $[CC(O)(CN)]^-$ unless fragmentation of this anion is preceded by rearrangement. Since the CA spectrum of $[CC(O)(CN)]^-$ (Fig. 2) is very similar to that of $[NCCCO]^-$ (Table 1), we propose that anion $[CC(O)(CN)]^-$ rearranges to $[NCCCO]^-$ preceding or during fragmentation. Thus we are unable to access neutral CC(O)(CN) by this route.

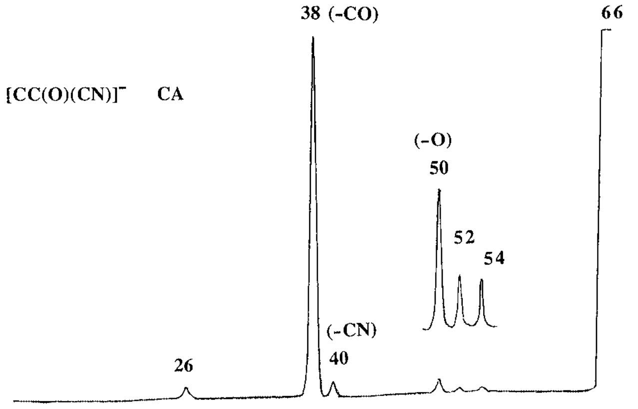


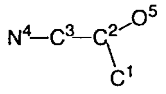
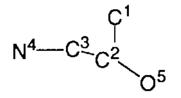
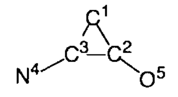
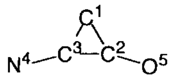
Fig. 2 Collisional activation (CA) mass spectrum (MS/MS) of $[CC(O)(CN)]^-$. VG ZAB 2HF mass spectrometer.

The rearrangement of $[CC(O)(CN)]^-$ to $[NCCCO]^-$

We have investigated the proposal that $[CC(O)(CN)]^-$ rearranges to $[NCCCO]^-$ using computational chemistry. Geometries have been determined at the B3LYP/6-31G(d) level of theory, while energies have been obtained using the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level. The results of these calculations are summarised in Fig. 3 and 4. The geometries of reactants and products are listed in Tables 2 and 3, while the geometries and energies of the transition states and intermediates shown in Fig. 3 and 4 are recorded in Table 4.

There are two states of $[C(O)(CN)]^-$ which are only 7 kJ mol^{-1} different in energy, *viz.* the singlet ground state and a low-lying triplet excited state. This is in marked contrast to the ground state singlet and the triplet state of $[NCCCO]^-$ which are 247 kJ mol^{-1} different in energy. Because of the similarity in energies of the singlet and triplet states of $[CC(O)(CN)]^-$, we have determined the reaction coordinates on both the singlet and triplet potential surfaces. We have not considered any possible interconversion between the two potential surfaces.

Table 4 Theoretical calculations for anionic transition states and intermediates shown in Fig. 3 and 4

	 Transition state A	 Transition state B	 Intermediate C	 Transition state D
State	1A′	$^3A''$	$^3A''$	$^3A''$
Symmetry	C_s	C_s	C_s	C_s
Energy/hartrees[a]	−244.1293682	−244.1092101	−244.1189378	−244.1186266
C^1C^2[b]/Å	1.360	1.417	1.428	1.429
C^2O^5/Å	1.295	1.246	1.228	1.223
C^2C^3/Å	1.480	1.470	1.525	1.659
C^3N^4/Å	1.169	1.210	1.258	1.237
C^1C^3/Å		1.822	1.470	1.447
$C^1C^2C^3$/°	115.5	78.2	59.6	55.3
$C^1C^2O^5$/°	121.4	146.0	152.4	149.4
$C^3C^2O^5$/°	123.1	135.8	148.0	155.3
$C^2C^3N^4$/°	179.7	167.5	148.3	145.7
$C^2C^1C^3$/°		52.2	63.4	70.5
$C^1C^3C^2$/°		49.6	56.9	54.3
$C^1C^3N^4$/°		142.9	154.7	160.1

[a] B3LYP/6-31G(d) level of theory including zero-point vibrational energy (calculated from vibrational frequencies and scaled by 0.9804[34]). [b] B3LYP/6-31G(d) level of theory.

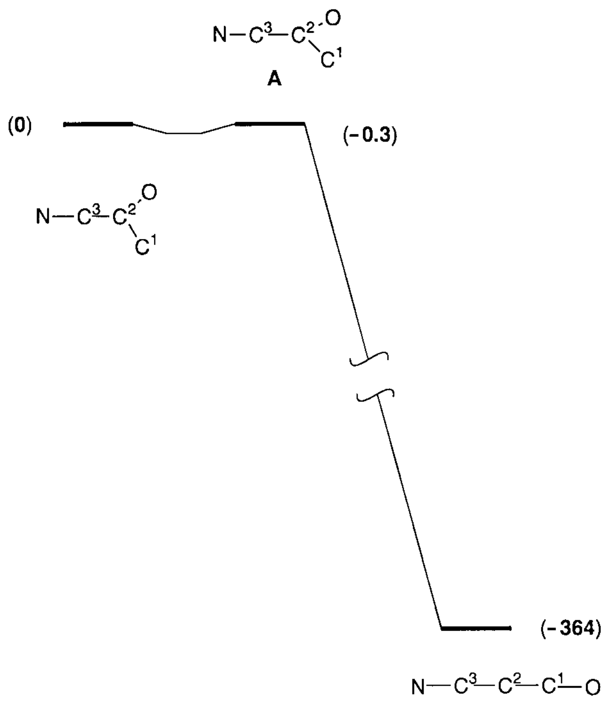


Fig. 3 Conversion of singlet $[CC(O)(CN)]^-$ to singlet $[NCCCO]^-$. Relative energies (in kJ mol^{-1}) at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. For full geometry and energy data see Tables 2–4.

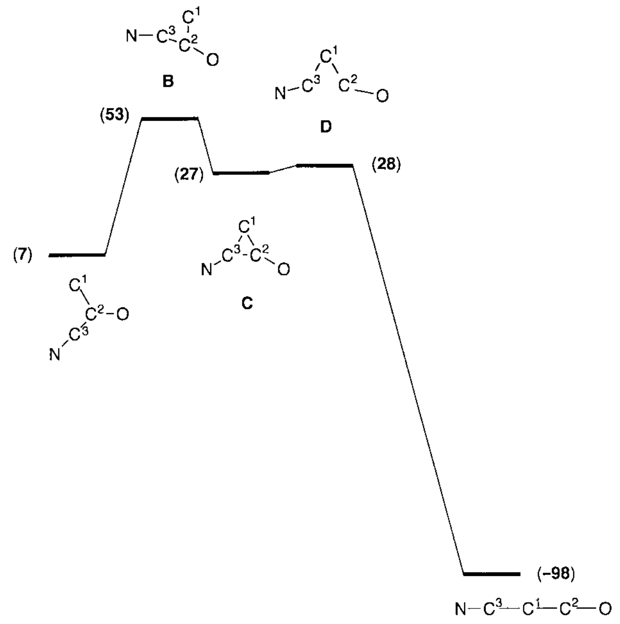


Fig. 4 Conversion of triplet $[CC(O)(CN)]^-$ to triplet $[NCCCO]^-$. Relative energies (in kJ mol^{-1}) at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. For full geometry and energy data see Tables 2–4. Triplet reactant $[CC(O)(CN)]^-$ has a relative energy of +7 kJ mol^{-1} with respect to singlet reactant $[CC(O)(CN)]^-$ (*cf.* Fig. 3).

The data in Fig. 3 show that the ground state singlet of $[CC(O)(CN)]^-$ is only theoretically stable because of a shallow barrier at −0.3 kJ mol^{-1}: after that the reaction to singlet $[NCCCO]^-$ is exothermic by 364 kJ mol^{-1} at the level of theory used. In practice, this means that singlet $[CC(O)(CN)]^-$ is likely to rearrange directly on formation to singlet $[NCCCO]^-$. The rearrangement of triplet $[CC(O)(CN)]^-$ to triplet $[NCCCO]^-$ (Fig. 4) is a stepwise process, which will proceed if the initial barrier of 53 kJ mol^{-1} can be surmounted. After that the energised system will proceed to triplet $[NCCCO]^-$, a reaction exothermic by 101 kJ mol^{-1}. The two mechanisms are different. The singlet mechanism involves oxygen rearrangement with no change to the connectivity of the carbon skeleton, while the triplet mechanism involves initial C^1–C^3 bond formation followed by C^2–C^3 bond cleavage to give triplet $[NCCCO]^-$ with a rearranged carbon backbone (see Fig. 3 and 4). Both rearrangements form $[NCCCO]^-$ with significant excess energy: this accounts for the pronounced fragment peaks observed in the CA spectrum of $[CC(O)(CN)]^-$ (see Fig. 2).

In conclusion

(a) The radical neutral NCCCO can be formed from $[NCCCO]^-$ without (i) scrambling of carbons of the cumulene system, or (ii) nitrile to isonitrile rearrangement.

(b) We were unable to form the neutral radical CC(O)(CN), because the precursor anion $[CC(O)(CN)]^-$ undergoes facile rearrangement to the more stable isomer $[NCCCO]^-$. However, theory suggests that neutral radical CC(O)(CN) should rearrange to neutral radical NCCCO.

(c) The singlet and triplet forms of $[CC(O)(CN)]^-$ both undergo facile rearrangement, in exothermic processes, to the respective singlet and triplet forms of $[NCCCO]^-$.

Experimental

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.[20] In summary, precursor anions $[NCCCO]^-$ and $[CC(O)(CN)]^-$ were prepared in the chemical ionization (CI) source of the mass spectrometer from reactions of $NCCH_2CO_2Me$ and $CH_2{=}C(OMe)(CN)$ respectively with HO^- (from H_2O) or $O^{-\bullet}$ (from N_2O).[21,22] The ions were accelerated to 7 keV translational energy and mass selected by means of the magnet. For collisional activation experiments,[23] 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.[24]

In neutralisation–reionisation experiments from anions to cations ($^-NR^+$),[25] the radical anions 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)[26–28] 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. The spectra were recorded a minimum of three times in order to establish their reproducibility.

Synthesis of precursor molecules

Methyl cyanoacetate was a commercial product and was used without purification. 1-Cyano-1-methoxyethylene[29] and methyl [^{13}C]cyanoacetate[30] ($^{13}C = 99\%$) were prepared by reported procedures.

Computational methods

Geometry optimizations were carried out with the Becke3LYP method[31,32] using the 6-31+G(d) basis within the GAUSSIAN94 suite of programs.[33] 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 scaled by 0.9804[34] and used for 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 aug-cc-pVDZ and aug-cc-pVTZ basis sets.[14,15] Calculations were carried out with the Power Challenge Super Computer at the Australian National University Super Computing Facility (Canberra).

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