# The Formation of the Neutral Isomers NCCCCO and CCC(O)CN in the Gas Phase from Ionic Precursors: a Joint Experimental and Theoretical Study

**Suresh Dua, Salvatore Peppe, and John H. Bowie***

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

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The two neutral radicals NCCCCO and CCC(O)CN have been made by collision-induced vertical one-electron reduction and oxidation (respectively) of the charged species $NCCCCO^+$ and $^-$ CCC(O)CN. The two charged precursors were prepared by the following reactions: (a) $[NC-C\equiv C-CO-CH_3]^{+\bullet} \rightarrow NCCCO^+ + CH_3^{\bullet}$ and (b) $(CH_3)_3Si-C\equiv C-CO-CN + F^- \rightarrow {}^-CCC(O)CN + (CH_3)_3SiF$. Neutral NCCCCO is a stable species, but when energized decomposes by loss of CO to form the radical CCCN [process endothermic by 38.5 kcal $mol^{-1}$: calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory]. Neutral CCC(O)CN is 46.8 kcal $mol^{-1}$ more positive in energy than the isomer NCCCCO. When energized, CCC(O)CN decomposes by loss of $NC^{\cdot}$ to form CCCO (process endothermic by 28.1 kcal $mol^{-1}$), but also undergoes a rearrangement process to produce NCCCCO, which is formed with excess energy and may decompose by loss of CO.

## Introduction

There are currently 121 molecules which have been detected (by either rotational or vibrational spectroscopy) in interstellar dust clouds and in circumstellar envelopes around carbon rich suns.[1] We have recently reported the syntheses of a number of stellar and potential stellar molecules in collision cells of a mass spectrometer, including cumulenes[2,3] and heterocumulenes,[2] some of which may be precursors of systems of biological importance. These molecules are normally produced by charge stripping of anions of known bond connectivity.[2] Heterocumulenes studied include $C_3O$,[4] $C_5O$ isomers,[5] $C_7O$,[6] $C_nO_n$ ($n = 2-6$),[7,8] NCN,[9] $NC_3N$,[9] and $NC_3O$.[10,11]

One of the interesting features of some neutral cumulenes is that, when energized, they may undergo reorganization of the carbon chain. For example, linear $C_4$ rearranges to the more stable rhombus $C_4$.[3] In the case of energized heterocumulene neutrals, rearrangement of both the heteroatom and the carbon chain may occur: for example $C_2COC_2$ rearranges to the more stable CCCCCO without causing scrambling of the carbon chain,[5] while NCCCN rearranges to CNCCN and also scrambles the carbons.[9] In contrast, CCCCCO and NCCCO undergo no rearrangement when energized; instead, they undergo loss of CO by simple cleavage to furnish CCCC[5] and NCC[11] respectively. These results suggests that if molecules of this type are formed in either interstellar dust clouds or circumstellar envelopes, there is the potential for their decomposition to form smaller molecules, or rearrangement to form other isomers.[2,5,9]

In the current study our aims are to extend our work on heterocumulenes (i) to form the two isomers NCCCCO and CCC(O)(CN) from ionic precursors of known bond connectivity, and (ii) to determine whether these isomers are stable species or whether they rearrange to other isomers.

## Experimental Section

**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.[12] In summary, precursor anions $[NCCCCO]^+$ and $[CCC(O)CN]^{-\bullet}$ were prepared in the chemical ionization (CI) source of the mass spectrometer by α cleavage of $[NCC\equiv CCOMe]^{+\bullet}$ and by the $S_N2(Si)$ reaction between $F^-$ (from $SF_6$) and $(CH_3)_3Si-C\equiv C-CO-CN$.[13] The ions were accelerated to 7 keV translational energy and mass selected by means of the magnet. For collisional activation experiments,[14] 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.[15]

In neutralization−reionization experiments ($-NR^+$ or $^+NR^+$),[16] the radical ions were neutralized 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. Reionization 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 ($^-CR^+$)[17−19] 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. Collision-induced mass spectra of cations were obtained similarly, except that Ar (80% T) was used as collision gas in the first of the two tandem collision cells. All spectra were recorded a minimum of three times in order to establish their reproducibility.

**B. Syntheses of Precursor Molecules.** The neutral precursors 1-cyano-3-methoxyprop-1-yne,[20] 4-cyanoprop-2-ynal,[20] and 2-oxo 4-cyanobut-3-yne[21] were prepared by reported methods.

1-Cyano-3-trimethylsilylprop-2-yne-1-one was prepared as follows: 3-trimethylsilylprop-2-ynoyl chloride $[(CH_3)_3Si-C\equiv C-CO-Cl]$ (0.5 g, 3.1 mM) in anhydrous methylene chloride (5 mL) was added dropwise over a 15 min period, at 0 °C, to

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* To whom correspondence should be addressed. Department of Chemistry, The University of Adelaide, South Australia. 5005 (e-mail: john.bowie@adelaide.edu.au).

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**TABLE 1: Theoretical Calculations for Anions, Cations, and Neutral of Linear $NC_4O$**

| | $N-C^1-C^2-C^3-C^4-O$ | | | | |
|---|---|---|---|---|---|
| | anion (singlet) | anion (triplet) | cation (singlet) | cation (triplet) | neutral (doublet) |
| state | $^1A'$ | $^3\Sigma$ | $^1\Sigma$ | $^3\Sigma$ | $^2A'$ |
| symmetry | $C_s$ | $C_{\infty v}$ | $C_{\infty v}$ | $C_{\infty v}$ | $C_s$ |
| energy (hartrees)[a] | −281.612651 | −281.616141 | −281.254583 | −281.139997 | −281.543634 |
| relative energy (kcal mol$^{-1}$) | 2.2 | 0 | 226.9 | 298.8 | 43.6 |
| dipole moment (debye) | 2.74 | 2.1 | 2.5 | 0.9 | 1.4 |
| bond length (Å)[b] | | | | | |
| $NC^1$ | 1.192 | 1.205 | 1.171 | 1.217 | 1.157 |
| $C^1C^2$ | 1.373 | 1.318 | 1.356 | 1.302 | 1.295 |
| $C^2C^3$ | 1.335 | 1.304 | 1.227 | 1.293 | 1.291 |
| $C^3C^4$ | 1.312 | 1.273 | 1.332 | 1.312 | 1.346 |
| $C^4O$ | 1.205 | 1.218 | 1.137 | 1.570 | 1.178 |
| angle (deg) | | | | | |
| $NC^1C^2$ | 164.2 | 180.0 | 180.0 | 180.0 | 170.9 |
| $C^1C^2C^3$ | 139.5 | 180.0 | 180.0 | 180.0 | 161.7 |
| $C^2C^3C^4$ | 140.6 | 180.0 | 180.0 | 180.0 | 155.7 |
| $C^3C^4O$ | 163.5 | 180.0 | 180.0 | 180.0 | 173.9 |
| $C^2C^3C^4O$ | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 |
| $C^1C^2C^3C^4$ | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 |
| $NC^1C^2C^3$ | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 |

[a] RCCSD(T)/aug-cc-pVDZ level of theory including zero-point vibrational energy [calculated from vibrational frequencies at B3LYP/6-31G* level of theory and scaled by 0.9804 (ref 25)]. [b] B3LYP/6-31G* level of theory.

a suspension of powdered aluminum chloride (0.8 g, 6.0 mM) in anhydrous dichloromethane (10 cm$^3$); the mixture was allowed to stir at 0 °C for 30 min, then filtered through glass wool under nitrogen. The filtrate was added dropwise over a 15 min period to a solution of trimethylsilylcyanide (0.31 g, 3.1 mM) in dichloromethane (5 mL) at 0 °C, and stirred at that temperature for 3 h. Sufficient aqueous hydrogen chloride (2 N) was added to dissolve the aluminum salts; the organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 20 cm$^3$). The combined organic extracts were concentrated and chromatographed on silica eluting with a chloroform/hexane mixture (1:1), to yield the required product as a yellow oil (0.28 g, 59%). $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$: 0.42 (s). IR (liquid): 1724, 2167 cm$^{-1}$. MS $[M^{+\bullet}-(CH_3)_3Si^\bullet]^+ = 78.0004$; $C_4NO$ requires 77.9980.

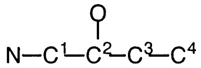
**C. Theoretical Methods.** Geometry optimizations were carried out with the Becke 3LYP method[22,23] using a modest 6-31G(d) basis within the GAUSSIAN 98 suite of programs.[24] Stationary points were characterized as either minima (no imaginary frequencies) or transition structures (one imaginary frequency) 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[25] by 0.9804 and used as a zero-point correction for the electronic energies calculated at this and higher levels of theory. B3LYP/6-31G(d) has previously been used for geometry optimizations of anionic carbon clusters and has demonstrated good correlation with structures calculated using high level coupled-cluster approaches.[26,27] Some problems have been highlighted in the literature regarding the use of the B3LYP method for the accurate prediction of molecular energies for carbon clusters,[28] even though the method continues to be used with success.[29,30] Consequently, more accurate energies for the B3LYP geometries were determined using the CCSD(T) method[31−36] together with the Dunning aug-cc-pVDZ basis set.[37,38] The CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) approach predicts the adiabatic electron affinity of linear $C_4$ to be 3.65 eV which is in reasonable agreement with the experimentally measured value of 3.88 eV.[39,40] We have addressed this matter in detail in the previous papers in this series.[11,41] All calculations were carried out on Power Challenge Supercomputers at either the South Australian Supercomputing Centre (Adelaide) or the Australian National University Supercomputing Facility (Canberra).

## Results and Discussion

**Formation of the Ionic Precursors of NCCCCO and CCC(O)CN and the Structures of the Two Neutrals.** In our previous study of $NC_3O$ isomers, we synthesized the radicals NCCCO and $N^{13}CCCO$ from the anionic precursors $[NCCCO]^-$ and $[N^{13}CCCO]^-$.[10,11] No rearrangement of the carbon chain was observed for the neutrals; instead, cleavage of CO formed NCC and $N^{13}CC$, respectively. We were unable to effect the synthesis of CC(O)CN from $[CC(O)CN]^{-\bullet}$ since the ground-state singlet anion, under conditions required for one-electron oxidation to the neutral, rearranged to the more stable $[NCCCO]^{-\bullet}$.[10,11] Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory show that this process involves a 1,2-oxygen rearrangement, proceeding over a minimal barrier in an exothermic reaction (−87 kcal mol$^{-1}$ at the level of theory used) to yield $[NCCCO]^-$.

Before commencing the syntheses of possible ionic precursors of the isomers NCCCCO and CCC(O)CN, we need to determine whether the cations and anions corresponding to these neutrals are stable. Our first preference, if possible, was to make the neutrals by one-electron vertical oxidation of the corresponding anions. The structures and relative energies of anions corresponding to NCCCCO and CCC(O)CN have been calculated at the respective B3LYP/6-31G(d) and CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) levels of theory: these data are summarized in Tables 1 and 2. These calculations indicate that there are stable singlet and triplet states of $[NCCCCO]^-$ on the anion potential surface. The linear triplet, which has significant cumulenic character, is the ground state. The bent singlet form is 2.2 kcal mol$^{-1}$ more positive in energy than the triplet at the level of theory used. There is also a stable singlet and a stable triplet of the isomer $[CCC(O)CN]^-$. However, in contrast to $[NCCCCO]^-$, the ground state of $[CCC(O)CN]^-$ is the singlet, which corresponds closely to the valence bond structure $^-C{\equiv}C-C(=O)-CN$. The triplet state of this isomer lies 13.4 kcal mol$^{-1}$ above the singlet ground state. We were unable to find

**TABLE 2: Theoretical Calculations for Anions, Cations, and Neutrals of Branched $NC_4O$**



| | anion (singlet) | anion (triplet) | cation (singlet) | cation (triplet) | neutral (doublet) |
|---|---|---|---|---|---|
| state | $^1A'$ | $^3A''$ | $^1A'$ | $^3A'$ | $^2A'$ |
| symmetry | $C_s$ | $C_s$ | $C_s$ | $C_s$ | $C_s$ |
| energy (hartrees)[a] | −281.489280 | −281.467809 | −281.067982 | −281.043655 | −281.469055 |
| relative energy (kcal mol$^{-1}$) | 0 | 13.5 | 264.4 | 279.6 | 12.7 |
| dipole moment (debye) | 3.76 | 2.29 | 1.35 | 4.53 | 1.87 |
| bond length (Å)[b] | | | | | |
| $NC^1$ | 1.165 | 1.178 | 1.168 | 1.166 | 1.162 |
| $C^1C^2$ | 1.504 | 1.408 | 1.393 | 1.422 | 1.467 |
| $C^2C^3$ | 1.397 | 1.409 | 1.442 | 1.426 | 1.442 |
| $C^3C^4$ | 1.261 | 1.280 | 1.247 | 1.239 | 1.247 |
| $C^2O$ | 1.239 | 1.314 | 1.216 | 1.240 | 1.216 |
| angle (deg) | | | | | |
| $NC^1C^2$ | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 |
| $C^1C^2C^3$ | 113.9 | 126.1 | 116.4 | 126.4 | 116.4 |
| $C^2C^3C^4$ | 180.0 | 180.0 | 180.0 | 164.4 | 180.0 |
| $C^3C^2O$ | 115.8 | 110.2 | 121.5 | 107.8 | 121.5 |
| $C^3C^2C^1O$ | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 |

[a] RCCSD(T)/aug-cc-pVDZ level of theory including zero-point vibrational energy [calculated from vibrational frequencies at B3LYP/6-31G* level of theory and scaled by 0.9804 (ref 25)]. [b] B3LYP/6-31G* level of theory.

**TABLE 3: Energetics of Possible Decomposition Pathways for Singlet and Triplet $[NCCCCO]^-$ and $[CCC(O)CN]^-$ (CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* Level of Theory)**

| reaction | energy (kcal mol$^{-1}$) |
|---|---|
| $^1[NCCCCO]^- \rightarrow {}^1[CCCN]^- + {}^1CO$ | −17.3 |
| $^3[NCCCCO]^- \rightarrow {}^3[CCCN]^- + {}^1CO$ | +92.2 |
| $^3[NCCCCO]^- \rightarrow {}^1[CCCN]^- + {}^3CO$ | +120.9 |
| $^1[NCCCCO]^- \rightarrow {}^2[CCCO]^{-\bullet} + {}^2NC^\bullet$ | +94.5 |
| $^1[NCCCCO]\text{-} \rightarrow {}^1[CCCO] + {}^1NC^-$ | +31.9 |
| $^1[NCCCCO]^- \rightarrow {}^3[CCCO]^{-\bullet} + {}^3NC^-$ | +225.8 |
| $^3[NCCCCO]^- \rightarrow {}^2[CCCO]^{-\bullet} + {}^2NC^\bullet$ | +96.7 |
| $^3[NCCCCO]^- \rightarrow {}^1[CCCO] + {}^3NC^-$ | +163.2 |
| $^3[NCCCCO]^- \rightarrow {}^3[CCCO] + {}^1NC^-$ | +98.9 |

any transition state for a 1,3-oxygen rearrangement of $[CCC(O)CN]^-$ to yield $[NCCCCO]^-$ (compare with the facile 1,2-oxygen rearrangement $[CC(O)CN]^-$ to $[NCCCO]^-$ [10,11]). These collective data suggest the two anionic precursors should be suitable candidates for the one-electron oxidation to form the appropriate neutral.

We have also carried out calculations for the corresponding cations $[NCCCCO]^+$ and $[CCC(O)CN]^+$ (Tables 1 and 2). Both of these isomeric cations have stable singlet and triplet states. The cumulenic triplet is the ground state of $[NCCCCO]^+$ by 1.7 kcal mol$^{-1}$, while the singlet is the ground state of $[CCC(O)CN]^+$ by 15.3 kcal mol$^{-1}$.

The molecular modeling studies outlined above suggest that the neutrals may be made either by one-electron oxidation from anion precursors, or by one-electron reduction from cationic precursors. Before proceeding with possible syntheses let us confirm that the two required neutrals are stable species. The data collected in Tables 1 and 2 show that both doublet neutral radicals are stable at the level of calculation used. The isomer NCCCCO is the global minimum on the neutral potential surface, being 46.8 kcal mol$^{-1}$ more negative in energy than the 'branched' isomer. The NCCCCO structure is not a simple linear cumulene like the corresponding $N{=}C{=}C{=}C{=}O$:[11] it is bent (see Table 1), but with significant cumulenic character. In contrast, the other isomer can be simply represented as the radical $^\bullet C{\equiv}C{-}C({=}O){-}C{\equiv}N$.

On the basis of the molecular modeling data outlined above, we decided to prepare both neutral isomers from anions of known bond connectivity, viz. (i), to prepare $[NCCCCO]^-$ by either deprotonation of an aldehyde (eq 1) or by the standard $O^{-\bullet}$ reaction shown in eq 2, and (ii) to form $[CCC(O)CN]^-$ from the neutral $(CH_3)_3Si{-}C{\equiv}C{-}CO{-}CN$ (eq 3). The third process involves a gas-phase $S_N2$(Si) reaction with $F^-$ (from $SF_6$) by a desilylation reaction of the type first reported by DePuy.[13]

$$N{\equiv}C{-}C{\equiv}C{-}CHO + NH_2^- \rightarrow [NCCCCO]^- + NH_3 \quad (1)$$

$$N{\equiv}C{-}C{\equiv}C{-}CH_2{-}OCH_3 + O^{-\bullet} \rightarrow [N{\equiv}C{-}C{\equiv}C{-}C{-}O{-}CH_3]^{-\bullet} + H_2O, \quad \text{then}$$

$$[N{\equiv}C{-}C{\equiv}C{-}C{-}O{-}CH_3]^{-\bullet} \rightarrow [NCCCCO]^- + CH_3^\bullet \quad (2)$$

$$(CH_3)_3Si{-}C{\equiv}C{-}CO{-}CN + F^- \rightarrow [CCC(O)CN]^- + (CH_3)_3SiF \quad (3)$$

The anion $[CCC(O)CN]^-$ is formed readily by the process shown in eq 3, but we were unable to form $[NCCCCO]^-$ by either of the processes shown in eqs 1 or 2. This is surprising, since both procedures appear to be quite straightforward. Although $[NCCCCO]^-$ is theoretically stable, it must not be stable under the experimental conditions that we have used for its formation: perhaps the triplet and singlet forms of the anion decompose by loss of CO or $^\bullet$CN? Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory have been carried out for the singlet and triplet forms of $[NCCCCO]^-$. The results are listed in Table 3.

The singlet $[NCCCCO]^-$ is only 2.2 kcal mol$^{-1}$ more positive in energy that the ground state triplet form (Table 1), so both singlet as well as triplet forms are likely to be accessible by the reactions shown in eqns 1 and 2. Loss of CO from singlet $[NCCCCO]^-$ is exothermic, which explains why this species is unstable under the experimental conditions used to form this species. The data shown in Table 3 indicate that all the decompositions of the triplet anion are strongly endothermic, which suggests that triplet $[NCCCCO]^-$ should be stable. Since we are unable to detect anions corresponding to NCCCCO, we suggest that the ground state triplet anion undergoes spin crossing to the singlet anion, which then decomposes by loss

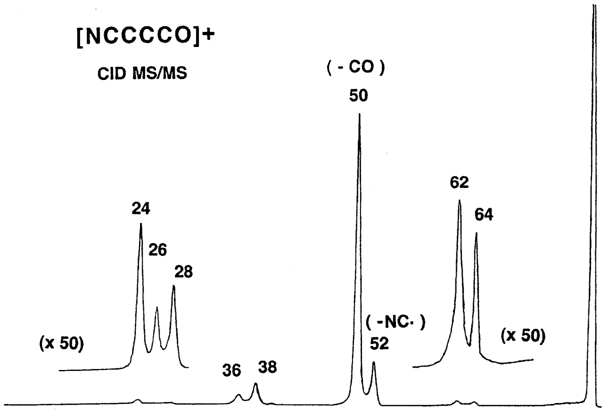


**Figure 1.** Collision-induced mass spectrum (MS/MS) of $[NCCCCO]^+$. VG ZAB 2HF mass spectrometer. Experimental conditions, see Experimental Section.

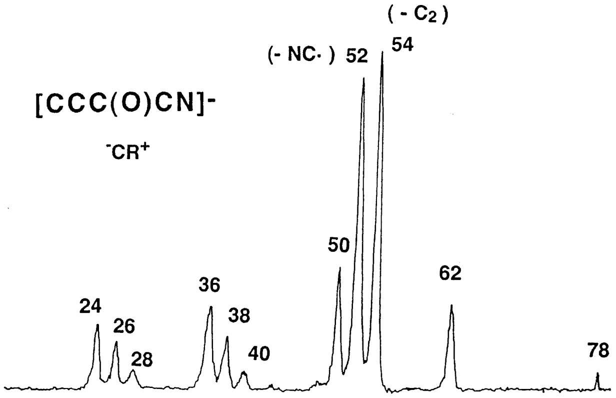


**Figure 2.** Charge reversal ($^-CR^+$) mass spectrum of $[CCC(O)CN]^-$. VG ZAB 2HF mass spectrometer. Experimental conditions, see Experimental Section.

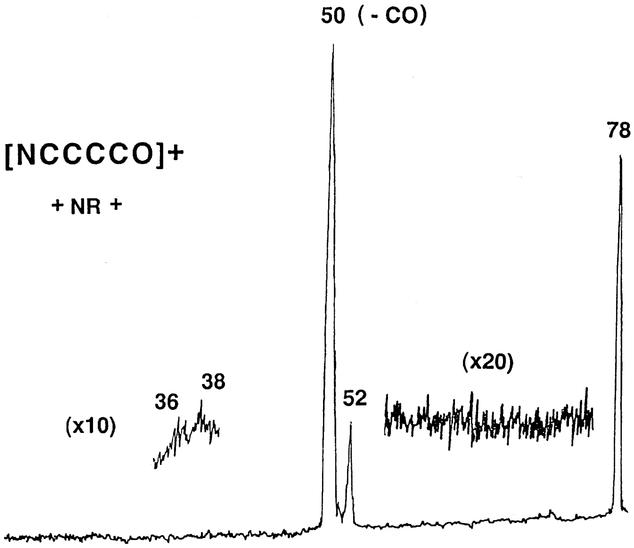


**Figure 3.** Neutralization/reionization ($^+NR^+$) mass spectrum of $[NCCCCO]^+$. VG ZAB mass spectrometer. Experimental conditions, see Experimental Section.

of CO. We have described such a process previously (for neutral OCCO[7]), and we calculate (by a reported method[42]) that the minimum energy cross over point between the triplet and singlet surfaces is only 0.2 kcal mol$^{-1}$ above the calculated singlet minimum (at the B3LYP/6-31G(d) level of theory). These data suggest that the ground-state triplet $[NCCCCO]^-$ will undergo facile spin inversion to form the singlet state provided the excess energy of the triplet anion is at least equal to the sum of the energy splitting between the triplet and singlet states plus 0.2 kcal mol$^{-1}$.[43]

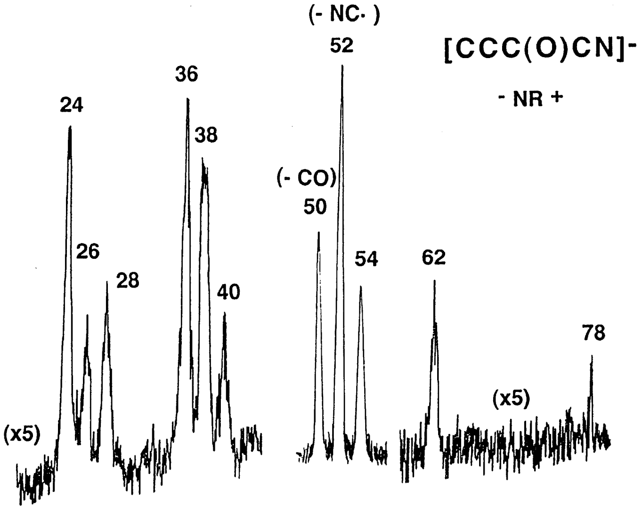


**Figure 4.** Neutralization−reionization ($^-NR^+$) mass spectrum of $[CCC(O)CN]^-$. VG ZAB 2HF mass spectrometer. Experimental conditions, see Experimental Section.

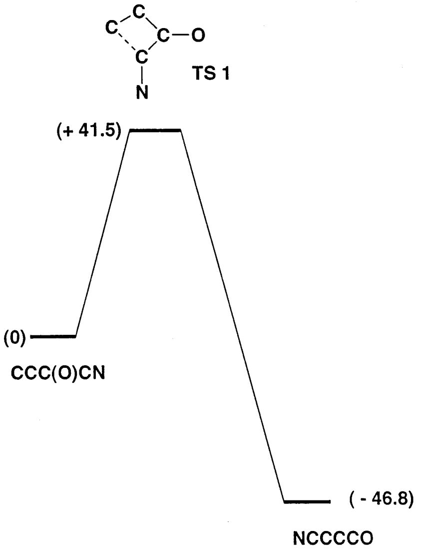


**Figure 5.** Rearrangement of neutral radical CCC(O)CN to NCCCCO. Concerted process. Geometries and energies at the B3LYP/6-31G(d) and CCSD(T)/aug-cc-pVDZ//B3LYP/6−31G(d) levels of theory, respectively. Relative energies in kcal mol$^{-1}$. For full details of geometries and energies, see Tables 1, 2, and 5.

$$[NC-C\equiv C-CO-CH_3]^{+\bullet} \rightarrow [NCCCCO]^+ + CH_3^{\bullet} \quad (4)$$

Thus we turned to the formation of NCCCCO by one-electron reduction from a cationic precursor; the proposed reaction is shown in eq **4**. This is a simple α cleavage process of a carbonyl radical cation system, and this reaction proceeds as expected.

The collisional induced mass spectrum of $[NCCCCO]^+$ and the charge reversal mass spectrum ($^-CR^+$)[17−19] of $[CCC(O)CN]^-$ are shown in Figures 1 and 2. The spectrum (Figure 1) of $[NCCCCO]^+$ is straightforward, showing major competitive losses of CO, $C_2O$ and $C_2N$. These fragmentations are in accord with the charged precursor having the bond connectivity NCCCCO. The charge reversal spectrum of $[CCC(O)CN]^-$ is particularly interesting. It shows peaks formed following major losses of $C_2$ and $NC^\bullet$ in accord with the bond connectivity

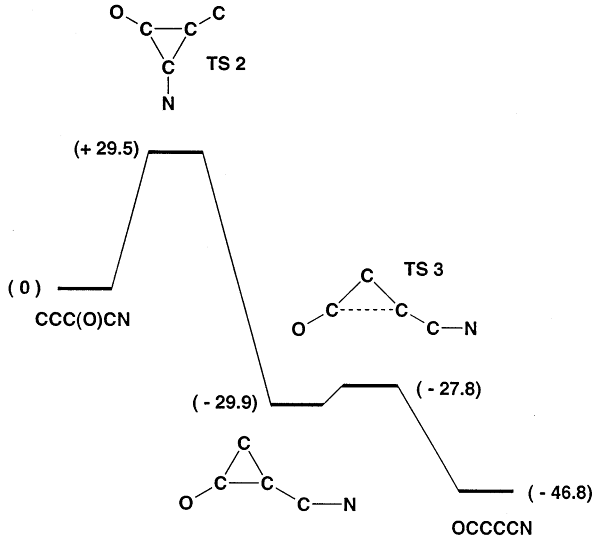


**Figure 6.** Rearrangement of neutral radical CCC(O)CN to NCCCCO. Stepwise process. Geometries and energies at the B3LYP/6-31G(d) and CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) levels of theory, respectively. Relative energies in kcal mol$^{-1}$. For full details of geometries and energies see Tables 1, 2, and 5.

CCC(O)CN. A minor peak due to loss of CO could indicate that some rearrangement (perhaps to [NCCCCO]$^+$) is occurring. This minor rearrangement in the spectrum of the cation [CCC(O)CN]$^+$ (formed by synchronous two electron stripping of the anion [CCC(O)CN]$^-$) means that under the experimental conditions used for the formation of the neutral radicals NCCCCO and CCC(O)CN from [NCCCCO]$^+$ and [CCC(O)CN]$^-$ any rearrangement of the cation [CCC(O)CN]$^+$ (perhaps to [NCCCCO]$^+$) is minimal.

**Formation of the Radicals NCCCCO and CCC(O)CN from [NCCCCO]$^+$ and [CCC(O)CN]$^{-\bullet}$.** The neutralization−reionization ($^+$NR$^+$) spectrum of [NCCCCO]$^+$ and the $^-$NR$^+$ spectrum of [CCC(O)CN]$^-$ are shown in Figures 3 and 4, respectively.[16] Figures 1 and 3 both exhibit peaks at $m/z$ 50 (−CO) and 52 (−NC$^\bullet$), with these peaks being more pronounced in the $^+$NR$^+$ spectrum (Figure 3). There is a pronounced recovery signal corresponding to the parent cation in the $^+$NR$^+$ spectrum indicating that some NCCCCO radicals are stable for the duration of the NR experiment (ca $10^{-6}$ s). The pronounced peak resulting from loss of CO in the $^+$NR$^+$ spectrum indicates that some of the NCCCCO neutrals are energized,[44] and decompose as shown in eq 5. This process is endothermic by 38.5 kcal mol$^{-1}$ at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.

$$\text{NCCCCO} \rightarrow \text{NCCC} + \text{CO} \tag{5}$$

The charge reversal ($^-$CR$^+$) spectrum of [CCC(O)CN]$^-$ (Figure 2) shows major formation of a decomposing [CCC(O)CN]$^+$ species with a minor amount of rearrangement. The neutralization−reionization spectrum of [CCCC(O)CN]$^-$ (Figure 4) shows a very small parent signal, which means that the neutrals CCC(O)CN mainly dissociate following or accompanying the vertical neutralization−reionization process. The signal produced by loss of $^\bullet$CN is much larger in the $^-$NR$^+$ than that in the $^-$CR$^+$ spectrum indicating that the major decomposition of neutral CCC(O)CN occurs by loss of NC$^\bullet$ as shown in eq 6, a process calculated to be endothermic by 28.1 kcal mol$^{-1}$ at the level of theory used in this study [the competitive loss of C$_2$ (eq 7) is endothermic by 89.7 kcal mol$^{-1}$]. The loss of CO in the $^-$NR$^+$ spectrum is slightly larger than that shown in the $^-$CR$^+$ spectrum indicating that neutral CCC(O)CN (like the corresponding cation) is undergoing minor rearrangement to a neutral isomer which dissociates by loss of CO.[45]

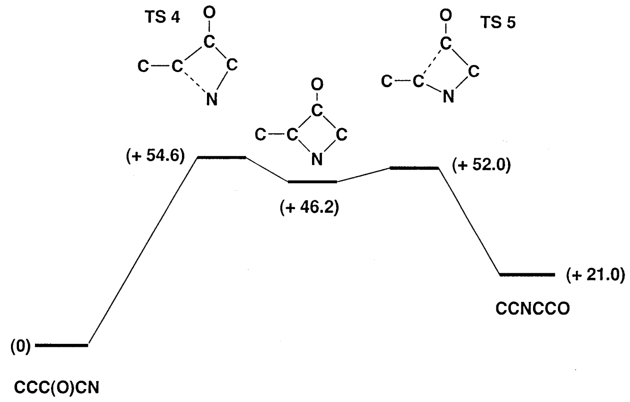


**Figure 7.** Rearrangement of neutral radical CCC(O)CN to CCNCCO. Geometries and energies at the B3LYP/6-31G(d) and CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) levels of theory, respectively. Relative energies in kcal mol$^{-1}$. For full details and geometries, see Tables 1, 2, 4 and 6.

**TABLE 4: Theoretical Calculations for Neutral C$_2$NC$_2$O**

| | $^1$C−C$^2$−N−C$^3$−C$^4$−O |
|---|---|
| | neutral |
| state | $^2A'$ |
| symmetry | $C_s$ |
| energy (hartrees)[a] | −281.4355815 |
| dipole moment (debye) | 2.6 |
| bond length (Å)[b] | |
| C$^1$C$^2$ | 1.306 |
| C$^2$N | 1.239 |
| NC$^3$ | 1.238 |
| C$^3$C$^4$ | 1.307 |
| C$^4$O | 1.176 |
| angle (deg) | |
| C$^1$C$^{2N}$ | 175.9 |
| C$^2$NC$^3$ | 166.7 |
| NC$^3$C$^4$ | 150.6 |
| C$^3$C$^4$O | 165.7 |
| OC$^3$C$^4$N | 180.0 |
| C$^2$NC$^3$C$^4$ | 180.0 |

[a] B3LYP/6-31G* level of theory including zero-point vibrational energy [calculated from vibrational frequencies and scaled by 0.9804 (ref 25)]. [b] B3LYP/6-31G* level of theory.

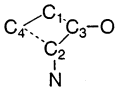
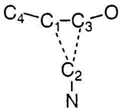
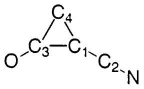
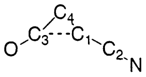
$$\text{CCC(O)CN} \rightarrow \text{CCCO} + \text{NC}^\bullet \tag{6}$$

$$\text{CCC(O)CN} \rightarrow \text{OCCN} + \text{C}_2 \tag{7}$$

We conclude that (i) we have prepared both of the neutral radicals NCCCCO and CCC(O)CN from ionic precursors, (ii) neutral NCCCCO is a stable species, but when energized may decompose by loss of CO, and (iii) neutral CCC(O)CN is less stable than the isomer NCCCCO under the reaction conditions used, principally decomposing by loss of NC$^\bullet$, but also undergoing some rearrangement to an isomer which decomposes by loss of CO. What is the structure of the isomer formed by rearrangement of CCC(O)CN?

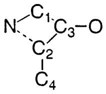
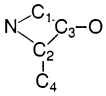
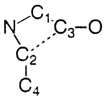
**Rearrangement of CCC(O)CN.** Potential surface calculations of rearrangements of CCC(O)CN system at the CCSD(T)/B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory are summarized in Figures 5 to 7. Details of geometries and energies of the neutrals NCCCCO, CCC(O)CN and CCNCCO are contained in Tables 1, 2, and 4 respectively, while those of

**TABLE 5: Transition State and Intermediate Structures on the Neutral Surface Shown in Figures 5 and 6**

| | <br>TS 1 | <br>TS 2 | <br>intermediate | <br>TS 3 |
|---|---|---|---|---|
| state | $^2A'$ | $^2A'$ | $^2A'$ | $^2A'$ |
| symmetry | $C_s$ | $C_s$ | $C_s$ | $C_s$ |
| energy (hartrees)[a] | −281.402881 | −281.422107 | −281.516693 | −281.513420 |
| bond lengths (Å)[b] | | | | |
| $C_1-C_3$ | 1.412 | 1.347 | 1.500 | 1.724 |
| $C_1-C_4$ | 1.318 | 1.327 | 1.346 | 1.338 |
| $C_2-C_3$ | 1.621 | 1.750 | | |
| $C_2-C_4$ | 1.650 | | | |
| $C_2-N$ | 1.239 | 1.174 | 1.167 | 1.174 |
| $C_3-O$ | 1.180 | 1.176 | 1.188 | 1.170 |
| $C_3-C_4$ | | | 1.436 | 1.390 |
| $C_1-C_2$ | | 1.754 | 1.394 | 1.370 |
| bond angles (deg) | | | | |
| $C_1-C_3-C_2$ | 65.3 | 67.6 | | |
| $C_3-C_2-C_4$ | 98.3 | | | |
| $C_1-C_4-C_2$ | 66.3 | | | |
| $C_3-C_1-C_4$ | 130.1 | 168.3 | 60.3 | 52.1 |
| $C_2-C_3-O$ | 143.6 | 128.3 | | |
| $C_3-C_2-N$ | 131.1 | 162.1 | | |
| $C_1-C_2-C_3$ | | 45.2 | | |
| $C_1-C_3-O$ | | 164.1 | 145.7 | 140.8 |
| $C_1-C_3-C_4$ | | | 54.5 | 49.5 |
| $C_1-C_2-N$ | | 152.7 | 176.7 | 174.3 |
| $C_2-C_1-C_3$ | | 67.2 | 144.3 | 151.3 |

[a] RCCSD(T)/aug-cc-pVDZ level of theory including zero-point vibrational energy [calculated from vibrational frequencies at B3LYP/6-31G* level of theory and scaled by 0.9804 (ref 25)]. [b] B3LYP/6-31G* level of theory.

**TABLE 6: Transition State and Intermediate Structures on the Neutral Surface Shown in Figure 7**

| | <br>TS 4 | <br>intermediate | <br>TS 5 |
|---|---|---|---|
| state | $^2A'$ | $^2A'$ | $^2A'$ |
| symmetry | $C_s$ | $C_s$ | $C_s$ |
| energy (hartrees)[a] | −281.381951 | −281.395393 | −281.386133 |
| bond lengths (Å)[b] | | | |
| $C_1-C_3$ | 1.568 | 1.582 | 1.520 |
| $C_1-C_4$ | | | |
| $C_2-C_3$ | 1.465 | 1.576 | 1.944 |
| $C_2-C_4$ | 1.313 | 1.316 | 1.293 |
| $C_2-N$ | 1.698 | 1.442 | 1.379 |
| $C_3-O$ | 1.187 | 1.175 | 1.157 |
| $C_1-N$ | 1.240 | 1.280 | 1.284 |
| bond angles (deg) | | | |
| $C_1-C_3-C_2$ | 84.7 | 77.8 | 70.4 |
| $C_3-C_2-C_4$ | 155.9 | 121.9 | 102.3 |
| $C_1-C_4-C_2$ | | | |
| $C_3-C_1-C_4$ | | | |
| $C_2-C_3-O$ | 138.9 | 141.6 | 144.0 |
| $C_3-C_2-N$ | 87.0 | 91.3 | 83.7 |
| $C_1-N-C_2$ | 86.7 | 93.4 | 99.0 |
| $C_3-C_1-N$ | 101.5 | 97.4 | 106.9 |

[a] RCCSD(T)/aug-cc-pVDZ level of theory including zero-point vibrational energy [calculated from vibrational frequencies at B3LYP/6-31G* level of theory and scaled by 0.9804 (ref 25)]. [b] B3LYP/6-31G* level of theory.

reactive intermediates and transition states shown in Figures 5−7 are listed in Tables 5 and 6.

There are two rearrangement pathways to NCCCCO: these are shown in Figures 5 and 6. The first (Figure 5) proceeds by concerted 1,4-C/C cyclization reaction, the second (Figure 6), by a stepwise process involving 1,3 C/C cyclization. Of the two processes, the latter is the more favored energetically. The maximum barrier for the stepwise process is 29.5 kcal mol$^{-1}$ above CCC(O)CN, and the product neutral NCCCCO, is 46.8 kJ mol$^{-1}$ more negative in energy than the other isomer. The rearrangement product NCCCCO formed in both reactions has significant excess energy (up to 76.3 and 88.3 kcal mol$^{-1}$ for the stepwise and concerted processes, respectively), and should readily lose CO, a reaction endothermic by 38.5 kcal mol$^{-1}$.

There is a further rearrangement process of CCC(O)CN which could, in principle, form a third isomer CCNCCO. This stepwise process is shown in Figure 7. This endothermic rearrangement has a higher barrier than either of the two processes shown in Figures 5 and 6. We have been unsuccessful in achieving an independent and unequivocal synthesis of the isomer CCNCCO. The rearrangement shown in Figure 7 is unfavorable compared with those shown in Figures 5 and 6.

In conclusion, energized CCC(O)CN prefers to decompose by loss of $^{\bullet}$CN rather than undergo rearrangement to NCCCCO. The rearrangement does occur, but it is only a minor process. We propose the rearrangement of CCC(O)CN forms NCCCCO principally by the stepwise process shown in Figure 5. Some of the species NCCCCO produced by this exothermic process will have sufficient excess energy to allow them to decompose by loss of CO to form CCCN.

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**Supporting Information Available:** Energetics of possible decomposition pathways for singlet and triplet $[NCCCCO]^+$ and $[CCC(O)CN]^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) A reviewer has suggested that if the reaction in eq 1 forms the singlet, this reaction is exothermic, and may contribute to the nonobservance of $[NCCCCO]^-$ by this route.

(44) Since the bond connectivities of $[NCCCCO]^+$ and NCCCCO are the same, the excess energy produced by the vertical ground to ground-state one-electron Franck−Condon reduction of cations to neutrals will carry through some of the excess energy of the precursor cation, some could be formed in excited states by the neutralisation process, and some neutrals once formed may undergo collisional activation in the collision cell. Thus some NCCCCO neutrals will be stable and be ionised in the second collision cell to give a parent cation, whereas others will decompose (e.g., see eq 5) to furnish other neutrals which in turn will be ionized in the second cell.

(45) A reviewer has requested similar data for cation decompositions, as those listed for anions in Table 3. These data are included in Table 7, as Supporting Information.