

Neutral cumulene oxide CCCCCO is accessible by one-electron oxidation of [CCCCO]^{-•} in the gas phase

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Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory indicate that doublet [CCCCO]^{-•} is a stable species which should undergo collision-induced Franck–Condon vertical oxidation under neutralisation–reionisation conditions (⁻NR⁺) to produce both triplet CCCCCO (ground state) and singlet CCCCCO. Some of the neutral CCCCCO species formed (particularly the triplet) should be stable for the microsecond duration of the NR experiment, whereas others will be energised (particularly the singlet) and should decompose to C₃ and CO. The [CCCCO]^{-•} radical anion has been formed in the ion source of the mass spectrometer by the reaction CH₃OCH₂C≡C–CO–CH(CH₃)₂ + O^{-•} → [CCCCO]^{-•} + CH₃O[•] + H₂O + (CH₃)₂CH[•]. The ⁻NR⁺ spectrum of [CCCCO]^{-•} shows a recovery signal at *m/z* 64 corresponding to ionised CCCCCO, together with a pronounced peak at *m/z* 36 (CCC⁺⁺) produced by ionisation of CCC (formed by the reaction CCCCCO → CCC + CO). The experimental observations are in agreement with the predictions of the theoretical study.

Introduction

Cumulenes and polycarbon monoxides have been detected in circumstellar envelopes which surround red giant stars and also in dark interstellar molecular clouds.^{1–3} Detected cumulenes include a number of C_{*n*} (*n* = 3 and 5), C_{*n*}H (*n* = 2–8) and C_{*n*}H₂ (*n* = 2–4 and 6) molecules.^{1–6} In contrast, there has been only limited detection of polycarbon monoxides. The linear species C₂O and C₃O [together with the associated propynal (HC≡C–CHO)] have been detected towards the dark molecular cloud TMC-1.^{7,8} Preliminary measurements suggest that C₅O may also be present, but this has yet to be confirmed.⁹ Linear C₅O has been synthesised from an anionic precursor.¹⁰ A number of theoretical studies have been devoted to polycarbon monoxides,^{11–15} and the photoelectron spectra of C₂O and C₃O have also been reported.¹⁶ The rotational spectra of C_{*n*}O (*n* = 2–9) have been detected in pyrolytic decomposition and pulsed discharge nozzle experiments.^{17–19}

It has been suggested that the mechanism of formation of the circumstellar molecules C₃O and propynal may be linked *via* ion molecule chemistry²⁰ or by photolysis of the cluster C₃·H₂O,^{21–23} and that the reaction C₃O^{•+} + H₂ → C₃HO⁺ + H[•] may provide a stellar pathway for the consumption of C₃O.²⁴ We have prepared the stable neutrals C₃O,²⁵ HCCCCO²⁶ and CCCHO²⁶ in the gas phase from charged precursors by means of neutralisation reionisation mass spectrometry. It was shown that energised CCCHO may rearrange to HCCCCO, which has sufficient excess energy of formation to effect dissociation to CO and C₂H,²⁶ and we have suggested that HCCCCO and CCCHO may co-occur with C₃O and HC≡C–CHO in dark molecular clouds.²⁶

In contrast to C₃ systems, few cumulenes containing four carbon atoms have been detected in interstellar dust clouds, circumstellar envelopes or regions of interstellar ice. The linear and rhombic isomers of C₄ have been described,²⁷ but these symmetrical species have not, as yet, been detected as stellar molecules. Neither have the cumulene oxides CCCCCO or HCCCCO, although spectroscopic and/or structural details of CCCCCO^{17,28–32} and HCCCCO isomers^{33–35} have been reported. The only C₄ cumulene to so far be detected in the stellar environment is HCCCCO.^{5,36}

The purpose of this investigation is to determine whether the radical anion [CCCCO]^{-•} can be made by an unequivocal

synthesis and if so whether this anion can be converted by one-electron Franck–Condon vertical oxidation to a stable neutral CCCCCO.

The anion [CCCCO]^{-•} has been studied previously. Theory predicts that it has a ²Π electronic state,^{28,31} confirmed by its absorption spectrum in a neon matrix.³² It is reported that this anion may be formed by the reaction of C₄^{-•} with oxygen.³⁷ However, this synthesis does not absolutely prove the bond connectivity of the product anion and as such is not suitable for this study. Therefore we need to develop a synthesis of [CCCCO]^{-•} of confirmed bond connectivity.

Results and discussion

The aim of this study is to attempt to make the target neutral CCCCCO by one-electron oxidation of the precursor anion [CCCCO]^{-•}, *i.e.* using the neutralisation–reionisation (⁻NR⁺) procedure.^{38–40} In this procedure the anion [CCCCO]^{-•} is converted to neutral CCCCCO by vertical one-electron oxidation. The neutral molecule is then, in turn, converted by one-electron oxidation to the cation radical [CCCCO]^{+•}. Some of these cations will be energised and the resulting decompositions may give an insight into the structure of the first formed neutral; *i.e.* is it CCCCCO, has it rearranged to another isomer, or has it decomposed to smaller neutral fragments?

This investigation is quite complex and uses experiment and theory in concert. We have chosen to report the theoretical aspects first, and then to show that the results of experiment are in accord with theory. The calculations used in the theoretical section of this paper were carried out at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Since the experimental procedure involves the sequence [CCCCO]^{-•} → CCCCCO → [CCCCO]^{+•}, the theoretical treatment follows this order.

A: The evidence based on theory

Possible rearrangements and decompositions of [CCCCO]^{-•}. The question that needs to be addressed first is whether [CCCCO]^{-•} is an appropriate precursor for CCCCCO. In other words will [CCCCO]^{-•} survive the collisional conditions necessary to convert it to the neutral CCCCCO or will it rearrange or decompose during these conditions?

Table 1 Energies (E in Hartrees),^a bond lengths (in Å),^b bond angles (in degrees)^b and dipole moments (Debye)^b of doublet anions

	1 ⁻	2 ⁻	3 ⁻	4 ⁻	5 ⁻	6 ⁻	7 ⁻	8 ⁻	9 ⁻
State	1 ⁻	2 ⁻	3 ⁻	4 ⁻	5 ⁻	6 ⁻	7 ⁻	8 ⁻	9 ⁻
Symmetry	² Π		² A''	² B ₁		² A''	² B ₂		
Energy	C _{sv} -226.94076	C ₁ -226.77552	C _s -226.80178	C _{2v} -226.90301	C ₁ -226.79557	C _s -226.85894	C _{2v} -226.78718	C ₁ -226.88785	C ₁ -226.78703
Dipole moment	4.36	4.47	2.52	3.11	3.14	2.97	3.18	2.34	0.39
C ¹ -C ²	1.263		1.267	1.289		1.262	1.295	1.359	1.292
C ¹ -C ⁴								1.649	1.573
C ² -C ³	1.337	1.341		1.496	1.350	1.367	1.561	1.576	1.573
C ² -C ⁴				1.496	1.350				
C ³ -C ⁴	1.281	1.288	1.267	1.361	1.558	1.374	1.295	1.350	
C ¹ -O	1.216	1.244		1.213	1.268			1.227	
C ² -O		1.316	1.324		1.483		1.409		
C ³ -O			1.324			1.379	1.409		1.386
C ⁴ -O			1.324			1.575			1.384
C ¹ -C ² -C ³	180.0								
C ² -C ³ -C ⁴	180.0	172.5		152.9	54.8	179.5	149.7	110.2	139.8
C ² -C ³ -O			172.1	62.9		157.0	149.7	69.0	92.5
C ¹ -C ² -O		170.7			124.5				
C ¹ -O-C ²			123.4						
C ² -O-C ³				180.0	144.6		56.4	138.1	94.4
C ³ -O-C ⁴						55.3			
O-C ¹ -C ²		133.3	172.1						
O-C ² -C ³									
O-C ³ -C ⁴									
O-C ⁴ -C ³									
C ¹ -C ² -C ³ -C ⁴				180.0		0.0	0.0	0.0	179.9
C ¹ -C ² -C ³ -O			180.0						
C ¹ -C ² -O-C ³									
C ¹ -O-C ² -C ³		179.9			-94.2				
C ² -C ³ -O-C ⁴						180.0			94.4
C ² -O-C ³ -C ⁴			180.0						
O-C ¹ -C ² -C ³				0.0			180.0		
O-C ² -C ³ -C ⁴		180.0							

^a CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory including zero-point energy (B3LYP/6-31G*, scaled by 0.9804).^b B3LYP/6-31G* level of theory.

There are a number of possible $[C_4O]^{-\bullet}$ isomers that, at least in principle, might be involved in the rearrangement of an energised $[CCCCO]^{-\bullet}$ anion radical. These are summarised in Scheme 1 with full details listed in Table 1. Most of these are high-energy species which do not need further consideration. There are however, two species which do require further investigation, namely the cyclic anion $4^{-\bullet}$ (99 kJ mol $^{-1}$) and the rhombic anion $8^{-\bullet}$ (139 kJ mol $^{-1}$). The reaction profile of the interconversion $1^{-\bullet} \rightarrow 4^{-\bullet} \rightarrow 8^{-\bullet}$ is shown in Fig. 1. Full geometries of the minima shown in Fig. 1 are contained in Table 1. Similar data for transition structures are listed in Table 2.

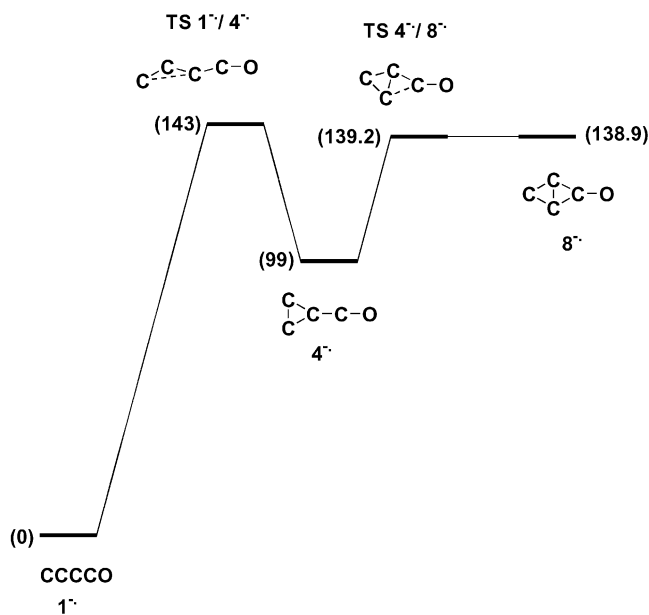
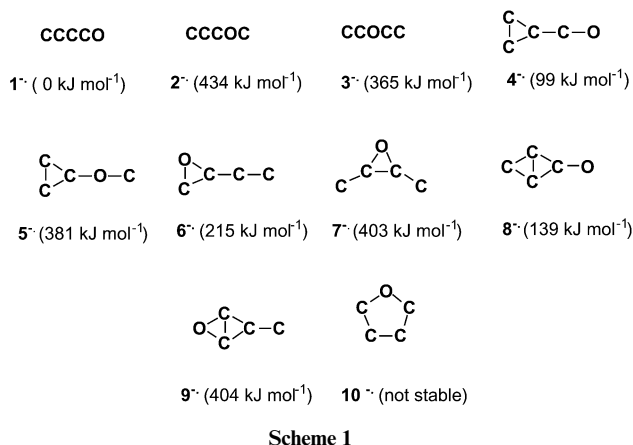


Fig. 1 Rearrangement of $1^{-\bullet}$ through $4^{-\bullet}$ to $8^{-\bullet}$. Calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Energies in kJ mol $^{-1}$ with respect to $1^{-\bullet}$ (0 kJ mol $^{-1}$).

Anion $1^{-\bullet}$ requires an excess energy of ≥ 143 kJ mol $^{-1}$ to convert through $4^{-\bullet}$ to the rhomboid structure $8^{-\bullet}$, in a reaction endothermic by 139 kJ mol $^{-1}$. Rearrangements of negative ions of this type are the exception rather than the rule;⁴¹ those that have been confirmed were for exothermic reactions with barriers ≤ 55 kJ mol $^{-1}$.⁴² It thus seems likely that $[CCCCO]^{-\bullet}$, once formed, should be stable under the collisional conditions required to effect the conversion of the anion to the neutral. In addition, decomposition of $[CCCCO]^{-\bullet}$ to $[CCC]^{-\bullet}$ and CO requires an excess energy of 151 kJ mol $^{-1}$ (Table 3). We conclude that $[CCCCO]^{-\bullet}$ is a suitable precursor for neutral CCCC.

Possible rearrangements and decompositions of neutral CCCC. There are stable singlet and triplet forms of CCCC,

with the triplet ground state being the more stable by 36 kJ mol $^{-1}$. Full details of both structures are listed in Tables 4 and 5. The results agree well with those obtained in previous studies.²⁸⁻³² For example, the electron affinity for triplet CCCC is calculated to be 2.86 eV [at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory], and this value should be compared with 2.83 eV at the CCSD/aug-cc-pVDZ level of theory.³¹ Both singlet and triplet CCCC are very similar in structure, and are best represented by the cumulene oxide structure C=C=C=O.

Since the triplet and singlet structures of CCCC are so similar in energy and geometry, it is necessary to study both the singlet and triplet potential surfaces of the C_4O system. Details of the relative energies of some triplet and singlet C_4O isomers [in comparison with that of triplet CCCC (nominally 0 kJ mol $^{-1}$)] are listed in Scheme 2. Full details of geometries and energies of these species are given in Tables 4 and 5. These isomers have been chosen because each, in principle, can be formed by rearrangement of energised CCCC. Relative energies of these isomers are shown in Scheme 2.

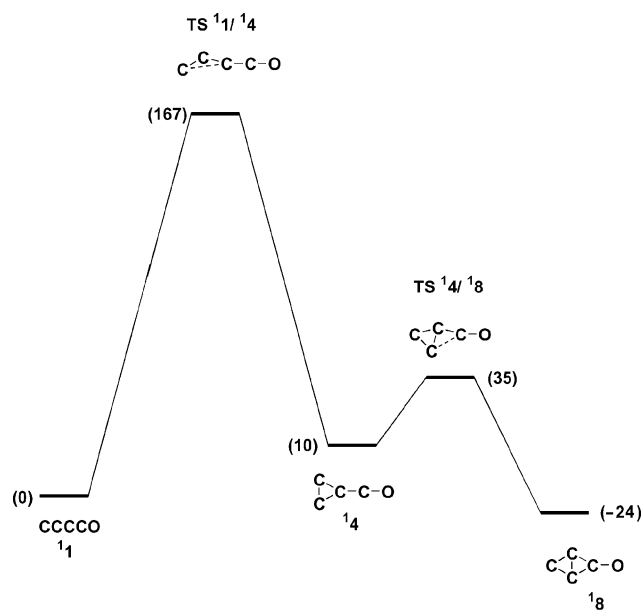
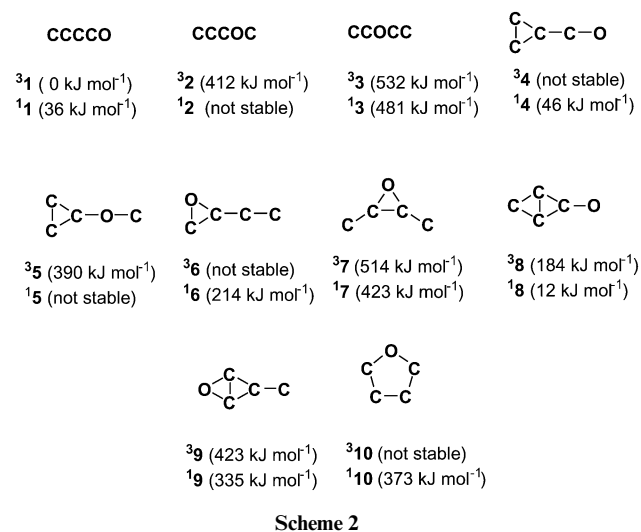
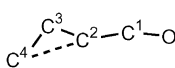
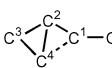


Fig. 2 Rearrangement of 1_1 through 1_4 to 1_8 . Calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Energies in kJ mol $^{-1}$ with respect to 1_1 (0 kJ mol $^{-1}$).

Triplet CCCC has the lowest energy of the isomers listed in Scheme 2. However, the triplet forms of the other isomers are either high-energy systems or unstable at the level of theory used

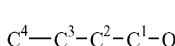
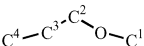
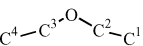
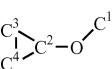
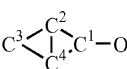
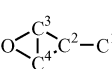
Table 2 Energies (E in Hartrees),^a bond lengths (in Å)^b and bond angles (in degrees)^b of transition states in Fig. 1

		
	TS 1 ⁻ /3 ⁻	TS 3 ⁻ /8 ⁻
State	² A'	² A'
Symmetry	C _s	C _s
Energy	-226.88640	-226.88774
C ¹ -C ²	1.266	1.345
C ¹ -C ⁴		1.750
C ² -C ³	1.423	1.541
C ² -C ⁴	1.970	
C ³ -C ⁴	1.313	1.354
C ¹ -O	1.224	1.213
C ¹ -C ² -C ³	175.5	119.5
C ² -C ³ -C ⁴	92.1	70.4
O-C ¹ -C ²	175.6	158.5
C ¹ -C ² -C ³ -C ⁴	0.0	0.0
O-C ¹ -C ² -C ³	180.0	180.0

^a CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory including zero-point energy (B3LYP/6-31G*, scaled by 0.9804).⁵⁰ ^b B3LYP/6-31G* level of theory.

for the calculations. Hence, triplet CCCCCO should not rearrange following neutralisation from [CCCCO]⁻. In contrast, the

Table 4 Energies (E in Hartrees),^a bond lengths (in Å),^b bond angles (in degrees)^b and dipole moments (Debye)^b of triplet neutrals

						
	³ 1	³ 2	³ 3	³ 5	³ 8	³ 9
State	³ Σ	³ A''	³ A''	C ₁	C ₁	³ A''
Symmetry	C _{∞v}	C _s	C _s	C ₁	C ₁	C _s
Energy	-226.83576	-226.67866	-226.63305	-226.68736	-226.76565	-226.67452
Dipole moment	2.32	3.78	0.66	0.62	1.42	1.22
C ¹ -C ²	1.288		1.297		1.508	1.322
C ¹ -C ⁴					1.508	
C ² -C ³	1.289	1.305		1.365	1.370	1.517
C ² -C ⁴				1.368		1.467
C ³ -C ⁴	1.314	1.304	1.297	1.389	1.370	
C ¹ -O	1.175	1.209		1.311	1.187	
C ² -O		1.322	1.262	1.370		
C ³ -O			1.262			1.294
C ⁴ -O						1.464
C ¹ -C ² -C ³	180.0				94.1	133.2
C ² -C ³ -C ⁴	180.0	171.8		59.3	84.5	
C ¹ -O-C ²		166.9		120.8		
C ¹ -C ² -O			172.8			
C ² -C ³ -O						100.6
C ² -O-C ³			153.5			
C ³ -O-C ⁴						85.9
O-C ¹ -C ²	180.0				142.3	
O-C ² -C ³		1.322		151.5		
O-C ³ -C ⁴			172.8			
C ¹ -C ² -C ³ -C ⁴					-26.9	
C ¹ -C ² -C ³ -O						180.0
C ¹ -C ² -O-C ³			180.0			
C ¹ -O-C ² -C ³		180.0		0.1		
C ² -C ³ -O-C ⁴			180.0			0.0
C ² -O-C ³ -C ⁴						
O-C ¹ -C ² -C ³					-151.5	
O-C ² -C ³ -C ⁴		180.0		180.0		

^a CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory including zero-point energy (B3LYP/6-31G*, scaled by 0.9804).⁵⁰ ^b B3LYP/6-31G* level of theory.

Table 3 Relative energies (in kJ mol⁻¹) for decomposition pathways of doublet anions 1⁻, 4⁻ and 8⁻

[CCCCO] ⁻ → CCC ⁻ + CO	151
[cyc-C ₃ CO] ⁻ → cyc-C ₃ ⁻ + CO	95
[rhm-C ₄ O] ⁻ → cyc-C ₃ ⁻ + CO	56

CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Energy values were determined from the following theoretically calculated values (Hartrees): CCC⁻ = -113.81418, CO = -113.06894, cyc-C₃⁻ = -113.79772, rhm-C₄⁻ = -151.76107, O = -74.92565.

singlet surface shows that the isomers **14** and **18** have relative energies of +10 kJ mol⁻¹ and -24 kJ mol⁻¹ with respect to singlet CCCCCO (**1**). Can **14** and **18** be formed from **11** during or following the one-electron oxidation of [CCCCO]⁻?

A simplified reaction profile of the rearrangement **11** → **14** → **18** is shown in Fig. 2. Full details of **11**, **14** and **18** are given in Table 5. The geometries and energies of the transition structures are shown in Table 6. Singlet CCCCCO needs an excess energy of ≥ 167 kJ mol⁻¹ for this reaction to proceed. If the reaction proceeds past the first transition state, **14** then has sufficient excess energy to pass the second transition state and form the rhombic species **18**. Singlet rhombus **18** is the global minimum on the singlet potential surface. We have noted previously that other rhomboid systems are also stable, e.g. rhombic C₄,²⁷ rhombic C₄C⁴³ and rhombic C₃BC.⁴⁴

The thermochemistry of possible decomposition processes of singlet and triplet CCCCCO are listed in Table 7. The lowest energy decomposition pathway corresponds to loss of CO in

Table 5 Energies (E in Hartrees),^a bond lengths (in Å),^b bond angles (in degrees)^b and dipole moments (Debye)^b of singlet neutrals

	1	3	4	6	7	8	9	10
State	¹ Π	¹ A''	¹ A ₁	¹ A'	¹ A ₁	¹ A ₁	¹ A ₁	¹ A ₁
Symmetry								
Energy	E_{SCF} -226.82200	E_{S} -226.65237	E_{SCF} -226.81810	E_{S} -226.75424	E_{SCF} -226.67478	E_{SCF} -226.83125	E_{SCF} -226.70810	E_{SCF} -226.69351
Dipole moment	2.12	1.37	2.60	2.44	0.98	0.69	0.99	0.51
C ¹ -C ²	1.290	1.293	1.332	1.286	1.321	1.468	1.307	1.426
C ¹ -C ⁴			1.428	1.311	1.436	1.468	1.505	1.340
C ² -C ³	1.292		1.428	1.451	1.427	1.427	1.505	1.340
C ² -C ⁴			1.434	1.451	1.321	1.427		1.489
C ³ -C ⁴	1.312	1.293	1.160		1.403	1.182		1.445
C ¹ -O	1.176	1.288		1.394	1.403		1.382	
C ² -O		1.288		1.358			1.381	1.369
C ³ -O								
C ⁴ -O								
C ¹ -C ² -C ³	180.0		149.8	176.6	151.9	114.2	138.5	141.0
C ² -C ³ -C ⁴	180.0		59.8	166.4	151.9	66.9	93.6	68.4
C ² -C ³ -O								
C ² -O-C ³		170.8						
C ² -O-C ⁴		126.9						
C ³ -O-C ⁴								
C ³ -O-C ¹								
O-C ¹ -C ²	180.0		180.0		59.2	147.6	86.7	134.2
O-C ² -C ³		170.8		56.4				92.2
O-C ³ -C ⁴								
O-C ⁴ -C ³								
C ¹ -C ² -C ³ -C ⁴								1.4
C ¹ -C ² -C ³ -O			180.0	0.0	0.0	0.0	-136.1	
C ¹ -C ² -O-C ³		180.0		180.0				
C ² -C ³ -O-C ⁴		180.0		180.0				
C ² -O-C ³ -C ⁴		180.0			180.0			
O-C ¹ -C ² -C ³			0.0		180.0	180.0		-24.2

^a CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory including zero-point energy (B3LYP/6-31G*, scaled by 0.9804).⁵⁰ ^b B3LYP/6-31G* level of theory.

Table 6 Energies (E in Hartrees),^a bond lengths (in Å)^b and bond angles (in degrees)^b of transition states in Fig. 2

	TS ¹ 1/ ¹ 4	TS ¹ 4/ ¹ 8
State	¹ A'	¹ A'
Symmetry	C _s	C _s
Energy	-226.75845	-226.80881
C ¹ -C ²	1.336	1.337
C ¹ -C ⁴		2.089
C ² -C ³	1.362	1.397
C ² -C ⁴	1.969	
C ³ -C ⁴	1.329	1.433
C ¹ -O	1.180	1.164
C ¹ -C ² -C ³	149.5	150.2
C ² -C ³ -C ⁴	94.0	66.5
O-C ¹ -C ²	158.5	169.5
C ¹ -C ² -C ³ -C ⁴	180.0	0.0
O-C ¹ -C ² -C ³	180.0	180.0

^a CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory including zero-point energy (B3LYP/6-31G*, scaled by 0.9804).⁵⁰ ^b B3LYP/6-31G* level of theory.

each case: ³1 and ¹1 require 256 and 19 kJ mol⁻¹ of excess energy in order to effect formation of CCC and CO. The singlet decomposition is a low-energy process and hence we need to know what excess energy is provided to the singlet as a consequence of the vertical one-electron oxidation. This quantity can be estimated from the difference in energy between the ground state neutral and the neutral with the anion geometry on the neutral potential surface. These calculations indicate that a singlet neutral has a Franck-Condon energy of 15 kJ mol⁻¹, an energy which is not sufficient to effect decomposition [19 kJ mol⁻¹ (Table 7)]. However, some of the singlet neutrals will experience higher internal energies due to either an initial high-energy collision or subsequent collision of the neutral. As a consequence, these neutrals may decompose to CCC and CO. In contrast, triplet neutral CCCCCO should be stable under the conditions of the experiment [calculated Franck-Condon energy of 19 kJ mol⁻¹: decomposition to ³CCC + CO requires 256 kJ mol⁻¹ (Table 7)].

The conclusions from this part of this theoretical investigation are: (i) vertical oxidation of [CCCCO]⁺ should yield some CC-CCO neutrals which are stable (mainly triplet), and some which decompose to CCC and CO (mainly singlet), (ii) rearrangement of CCCCCO should not be observed, and (iii) the triplet should be stable under the experimental conditions, while the singlet will decompose to form CCC and CO provided it has an excess energy of ≥19 kJ mol⁻¹.

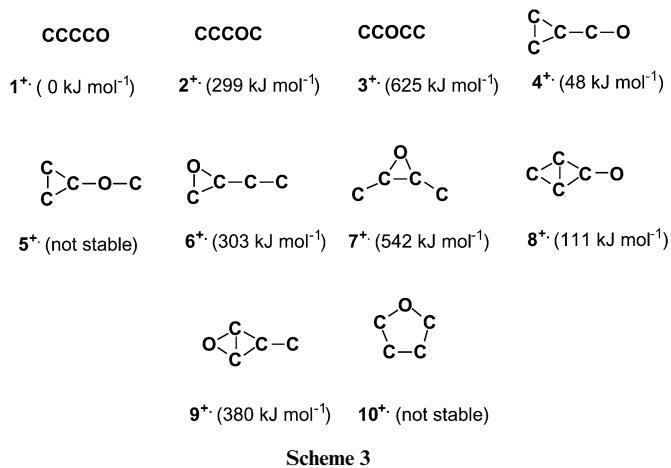
Table 7 Relative energies (in kJ mol⁻¹) for decomposition pathways of singlet and triplet neutral CCCCCO

¹ CCCCO → ¹ CCC + CO	19
¹ CCCCO → ¹ CCCO + ¹ C	500
¹ CCCCO → ³ CCCC + O	691
³ CCCCO → ³ CCC + CO	256
³ CCCCO → ¹ CCCO + ³ C	385
³ CCCCO → ¹ CCCC + O	660

CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Energy values were determined from the following theoretically calculated values (Hartrees): ¹CCC = -113.74598, ³CCC = -113.66924, CO = -113.06894, ¹CCCO = -188.92411, ¹C = -37.70756, ³C = -37.76487, ¹CCCC = -151.65881, ³CCCC = -151.63301, O = -74.92565.

Possible rearrangements and decompositions of [CCCCO]⁺.

The relative energies of isomeric doublet cation radicals are summarised in Scheme 3, with full details listed in Table 8. Most of the isomeric cation radicals are either unstable or of high energy with respect to ¹1⁺ (0 kJ mol⁻¹). However, in common with data for the analogous anions and neutrals, the exceptions are ⁴1⁺ (48 kJ mol⁻¹) and ⁸1⁺ (111 kJ mol⁻¹).



The reaction coordinate profile for the rearrangement ¹1⁺ → ⁴1⁺ → ⁸1⁺ is shown in Fig. 3. Full details of minima and transition structures shown in Fig. 3 are given in Tables 8 and 9. The rearrangement of ¹1⁺ through ⁴1⁺ to ⁸1⁺ has a maximum barrier of 111 kJ mol⁻¹. The overall reaction sequence is endothermic by 111 kJ mol⁻¹. The energetics of this process are within the energy range of cation rearrangements that have been reported previously (*e.g.* ref. 27). Possible decompositions of the cation radicals shown in Fig. 3 are listed in Table 10. These are all high-energy processes and will not compete with the rearrangement process shown in Fig. 3.

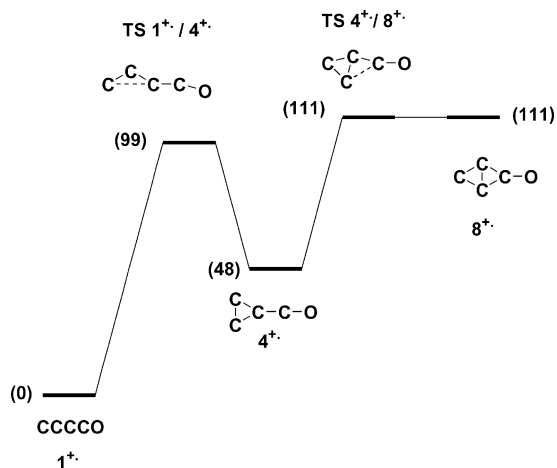


Fig. 3 Rearrangement of ¹1⁺ through ⁴1⁺ to ⁸1⁺. Calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Energies in kJ mol⁻¹ with respect to ¹1⁺ (0 kJ mol⁻¹).

The conclusions of the theoretical study are as follows:

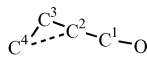
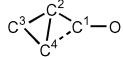
- (1) [CCCCO]⁺ is an appropriate precursor for CCCCCO.
- (2) Vertical oxidation of [CCCCO]⁺ should yield some CCCCCO neutrals which, depending on their internal energies, are either stable or decompose to CCC and CO.
- (3) The [CCCCO]⁺ cation formed from CCCCCO is stable, but rearrangement to the *cyclo*-C₃ [⁴1⁺] and rhomboid [⁸1⁺] cations occurs below the calculated lowest energy dissociation pathways for ¹1⁺, ⁴1⁺ and ⁸1⁺.

Table 8 Energies (E in Hartrees),^a bond lengths (in Å),^b bond angles (in degrees)^b and dipole moments (Debye)^b of doublet cations

	1⁺⁺	2⁺⁺	3⁺⁺	4⁺⁺	6⁺⁺	7⁺⁺	8⁺⁺	9⁺⁺
State	² Π			² A'	² A'	² A'	² A ₁	
Symmetry								
Energy	$C_{\infty v}$ -226.49135	C_1 -226.37736	C_1 -226.25330	C_s -226.47299	C_s -266.37604	C_s -226.28491	C_{3v} -226.44899	C_1 -226.34660
Dipole moment	0.22	9.05	12.34	8.51	0.59	7.65	2.86	8.66
C ¹ -C ²	1.332	1.335	1.335	1.375	1.336	1.347	1.511	1.355
C ¹ -C ⁴				1.328	1.284	1.392	1.511	1.457
C ² -C ³	1.253	1.227		1.527	1.499	1.428	1.344	1.457
C ² -C ⁴			1.317	1.409	1.499	1.428	1.344	
C ³ -C ⁴	1.369	1.337	1.317	1.334	1.410	1.511	1.159	
C ¹ -O	1.143	1.178	1.241		1.290	1.314		1.360
C ² -O	1.442	1.261	1.261					1.360
C ³ -O								
C ⁴ -O								
C ¹ -C ² -C ³	180.0			158.1	167.0	162.8	110.4	141.9
C ² -C ³ -C ⁴	180.0	166.1	67.8	67.8	167.3	150.0	74.3	99.9
C ² -C ³ -O			153.8					
C ¹ -O-C ²		157.6	156.1					
C ² -O-C ³								
C ³ -O-C ⁴								
O-C ¹ -C ²				178.7		53.6	147.5	82.1
O-C ² -C ³	180.0	127.3	151.3					
O-C ³ -C ⁴					60.2			
O-C ³ -C ³								
C ¹ -C ² -C ³ -C ⁴				180.0	0.0	0.0	0.0	161.0
C ¹ -C ² -C ³ -O								
C ¹ -C ² -O-C ³			-141.9					
C ¹ -O-C ² -C ³		179.9			180.0			
C ² -C ³ -O-C ⁴			126.8		180.0			12.2
C ² -O-C ³ -C ⁴				180.0		180.0	180.0	
O-C ¹ -C ² -C ³								
O-C ² -C ³ -C ⁴		-180.0						

^a CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory including zero-point energy (B3LYP/6-31G*, scaled by 0.9804).³⁰ ^b B3LYP/6-31G* level of theory.

Table 9 Energies (E in Hartrees),^a bond lengths (in Å)^b and bond angles (in degrees)^b of transition states in Fig. 3

		
	TS 1 ⁺ */4 ⁺ *	TS 4 ⁺ */8 ⁺ *
State	² A'	² A'
Symmetry	C _s	C _s
Energy	-226.45376	-226.44905
C ¹ -C ²	1.335	1.404
C ¹ -C ⁴		1.824
C ² -C ³	1.304	1.328
C ² -C ⁴	1.998	
C ³ -C ⁴	1.362	1.362
C ¹ -O	1.149	1.147
C ¹ -C ² -C ³	170.7	125.2
C ² -C ³ -C ⁴	97.1	76.3
O-C ¹ -C ²	175.3	161.3
C ¹ -C ² -C ³ -C ⁴	180.0	0.0
O-C ¹ -C ² -C ³	180.0	180.0

^a CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory including zero-point energy (B3LYP/6-31G*, scaled by 0.9804).⁵⁰ ^b B3LYP/6-31G* level of theory.

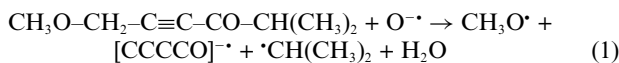
Table 10 Relative energies (in kJ mol⁻¹) for decomposition pathways of doublet cations 1⁺*, 4⁺* and 8⁺*

[CCCCO] ⁺ * → CCC ⁺ * + CO	295
[cyc-C ₃ CO] ⁺ * → cyc-C ₃ ⁺ * + CO	261
[rhm-C ₄ O] ⁺ * → cyc-C ₃ ⁺ * + CO	198
[rhm-C ₄ O] ⁺ * → rhm-C ₄ ⁺ * + O	665

CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Energy values were determined from the following theoretically calculated values (Hartrees): CCC⁺* = -113.31012, CO = -113.06894, cyc-C₃⁺* = -113.30453, rhm-C₄⁺* = -151.27022, O = -74.92565.

B: The evidence based on experiment

The anion [CCCCO]^{-*} was made in modest yield by the process shown in eqn. (1). This is a standard process involving the reaction of O^{-*} (from N₂O)⁴⁵ with an 'activated' CH₂ group to effect loss of water. The eliminations of CH₃O^{-*} and (CH₃)₂CH^{-*} follow or accompany the expulsion of water.



The collision induced (CID) negative ion mass spectrum of [CCCCO]^{-*} shows only a minor loss of CO, a decomposition in accordance with the bond connectivity shown and with theoretical data which predict that [CCCCO]^{-*} should not rearrange under CID conditions. The ⁻CR⁺ (direct conversion of [CCCCO]^{-*} to [CCCCO]^{4+*}) and ⁻NR⁺ (stepwise conversion of [CCCCO]^{-*} to CCCCCO to [CCCCO]^{4+*}) spectra of [CCCCO]^{-*} are shown in Fig. 4.

The ⁻CR⁺ spectrum (Fig. 4(A)) shows competitive losses of C, O, CC, CO, CCC and CCO from the molecular cation. These fragmentations are consistent with structure [CCCCO]^{4+*} (1⁺*), but some of these fragmentations (e.g. loss of O and CO) could also originate from energised isomers 4⁺* or 8⁺*. Since the anions 4^{-*} or 8^{-*} cannot be made by conventional syntheses, we are unable to compare the ⁻CR⁺ spectra of anions 1^{-*}, 4^{-*} and 8^{-*}. The ⁻NR⁺ spectrum (Fig. 4(B)) is weak and some minor fragment ions are difficult to see above baseline noise. Even so, the losses of C, O and CO are observed in both the ⁻NR⁺ the ⁻CR⁺ spectra. The peak at m/z 36 is more pronounced in the ⁻NR⁺ spectrum, a consequence of the facile loss of CO from singlet CCCCCO (see Table 7). The recovery signal (m/z 64) in

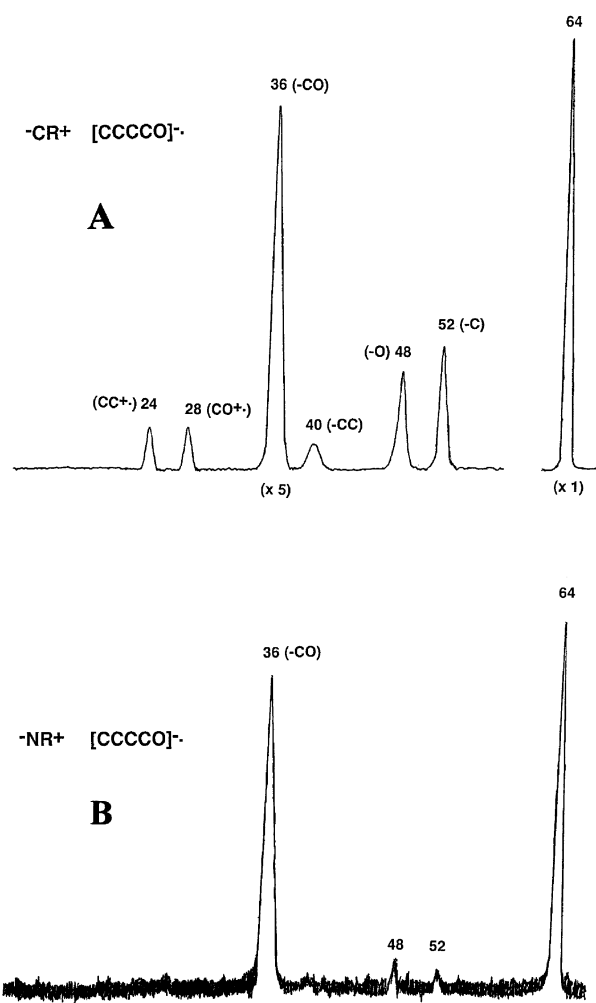


Fig. 4 (A) ⁻CR⁺ spectrum of [CCCCO]^{-*}; VG ZAB 2HF mass spectrometer. (B) ⁻NR⁺ spectrum of [CCCCO]^{-*}; HF-ZAB/AMD 604 mass spectrometer.^{27,57}

the ⁻NR⁺ spectrum is consistent with some neutral CCCCCO molecules being stable for the microsecond duration of the NR experiment.

In conclusion, a combination of experiment and theory has shown that neutral CCCCCO is accessible by one-electron oxidation of [CCCCO]^{-*}. Some of the CCCCCO neutrals are stable for the microsecond duration of the NR experiment, others are energised and decompose to form CCC and CO.

Theoretical and experimental details

A: Theoretical methods

Geometry optimisations were carried out with the Becke 3LYP method^{46,47} using the Dunning aug-cc-pVDZ basis set⁴⁸ within the GAUSSIAN 98 suite of programs.⁴⁹ Stationary points were characterised as minima (no imaginary frequencies). The calculated frequencies were also used to determine zero-point vibrational energies which were used as a zero-point correction for the electronic energies. These were scaled by 0.9804.⁵⁰ We have previously reported the success of the B3LYP method in predicting geometries of unsaturated chain structures, and that this method produces optimised structures, at low computational cost, that compare favourably with higher level calculations.⁵¹ More accurate energies for the B3LYP geometries were determined using the couple cluster CCSD(T) method⁵² using the Dunning aug-cc-pVDZ basis set.⁴⁸ All calculations were carried out on the Alpha Server at the Australian Partnership for Advanced Computing (APAC) National Facility (Canberra).

B: Mass spectrometric methods

A detailed description of the instrument used is given in ref. 26. In brief, the experiments were performed using a two-sector modified VG ZAB 2HF mass spectrometer with BE configuration, where B and E represent magnetic and electric sectors, respectively. The precursor anion [CCCCO]⁻ was formed in the chemical ionisation source by the reaction between O⁻ (from N₂O⁴⁵) and CH₃OCH₂C≡C-CO-CH(CH₃)₂ as shown in eqn. (1). CH₃OCH₂C≡C-CO-CH(CH₃)₂ was prepared by a reported procedure.⁵³

Typical source conditions were as follows: source temperature 200 °C, repeller voltage -0.5 V, ion extraction voltage 7 kV, mass resolution $m/\Delta m \geq 1500$. Each neutral precursor was inserted into the ion source through the septum inlet, which was heated to 60 °C to give a measured pressure of ca. 10⁻⁶ Torr inside the source housing. The reagent gas [N₂O (for O⁻)] was introduced through a gas inlet into the ion source to a measured total pressure of ca. 10⁻⁵ Torr in the source housing. The estimated total pressure in the ion source is 10⁻¹ Torr. The collisional induced dissociation (CID) spectrum was determined using B to select the parent anion, and utilising argon as the target gas in the first collision cell following B. The pressure of argon in the first cell was maintained such that 80% of the parent ion beam was transmitted through the cell. This corresponds to an average of 1.1–1.2 collisions per ion.⁵⁴ Product anion peaks resulting from CID processes were recorded by scanning E. The charge reversal (-CR⁺) spectrum^{55,56} was recorded using single collision conditions in collision cell 1 (O₂, 80% transmission of main beam).

We were unable to obtain a satisfactory neutralisation–reionisation (-NR⁺)^{38–40} spectrum of [CCCCO]⁻ with the ZAB 2HF instrument (Adelaide), so this spectrum was measured using the ZAB/AMD 604 mass spectrometer (Technical University, Berlin). Full details of this instrument have been outlined previously.^{27,57} Neutralisation of anions was effected by collisional electron detachment using O₂ at 80% transmittance (of the main beam) as the collision gas in the first collision cell, while reionisation to cations was achieved by collision of the neutrals with O₂, (80% transmittance) in a second collision cell.

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