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One-electron oxidation of $[CCOCC]^{-\bullet}$ in the gas phase forms stable and decomposing forms of CCCCO

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The radical anion $[CCOCC]^{-\bullet}$ may be made in the source of a VG ZAB 2HF mass spectrometer by the reaction between F^- (from SF_6) and $(CH_3)_3SiC{\equiv}COC{\equiv}CSi(CH_3)_3$. Vertical (Franck–Condon) one-electron oxidation of $[CCOCC]^{-\bullet}$ in the first collision cell produces both singlet and triplet CCOCC. A combination of experiment and molecular modelling (at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory) gives data which are consistent with the CCOCC neutrals rearranging over small barriers to form singlet and triplet CCCCO in exothermic reactions. Both singlet and triplet CCCCO formed in this way have excess energy. Singlet CCCCO has sufficient excess energy to effect decomposition exclusively to CCC and CO. In contrast, some of the triplet CCCCO neutrals are stable, while others decompose to CCC and CO.

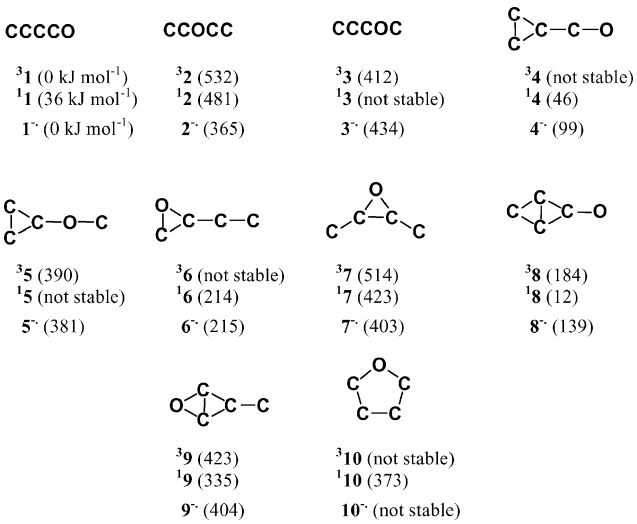
Introduction

There has been only limited detection of polycarbon monoxides (cumulene oxides) in circumstellar envelopes which surround red giant stars and in dark interstellar molecular clouds.[1–6] The linear species C_2O and C_3O [together with the associated propynal ($HC{\equiv}C–CHO$)] have been detected towards the dark molecular cloud TMC-1,[5,6] while preliminary measurements suggest that C_5O may also be present, but this has yet to be confirmed.[7] Linear C_5O has been synthesised from an anionic precursor.[8] A number of theoretical studies have been devoted to polycarbon monoxides,[9–12] and the photoelectron spectra of C_2O and C_3O have been determined.[13] The rotational spectra of C_nO ($n = 2$–9) have been detected in pyrolytic decomposition and pulsed discharge nozzle experiments.[14–17] Some spectroscopic and/or structural details of CCCCO have been reported.[11,15,18–23]

Neutral CCCCO has not been detected in circumstellar envelopes or molecular clouds, but it seems likely that it should be an interstellar molecule since the C_2, C_3 and C_5 analogues have been so identified. The anion radical precursor of CCCCO may be formed in the ion source of a mass spectrometer by the reaction between $O^{-\bullet}$ and $CH_3OCH_2C{\equiv}C–CO–CH(CH_3)_2$, and Franck–Condon vertical one-electron oxidation of $[CCCCO]^{-\bullet}$ gives stable triplet and decomposing singlet forms of CCCCO.[23] In the course of that study, the structures and energies of the singlet and triplet forms of nine C_4O isomers (that in principle, might be formed by isomerisation of CCCCO) were determined at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. These are summarised in Scheme 1. All energies are relative to triplet CCCCO (0 kJ mol^{-1}). Apart from CCCCO, the only other neutral isomer (shown in Scheme 1) that can be formed experimentally from a readily accessible anionic precursor of known connectivity is CCOCC. The synthesis of the required precursor $[CCOCC]^{-\bullet}$ should be straightforward, using the Squires modification[25] of the DePuy $SN_2(Si)$ reaction.[24] In this case the process involves the reaction between F^- and $(CH_3)_3SiC{\equiv}C–O–C{\equiv}CSi(CH_3)_3$ to yield the products $[CCOCC]^{-\bullet}$ and $(CH_3)_3SiF$.

The aims of this project are:

(i) To synthesise $[CCOCC]^{-\bullet}$ by an unequivocal route and to determine whether this radical anion is an appropriate precursor for the formation of neutral CCOCC, and (ii) following (i) above, to subject $[CCOCC]^{-\bullet}$ to Franck–Condon vertical one-electron oxidation, and to determine whether the first formed neutral species CCOCC is stable under the conditions of the neutralisation experiment, or whether it either decomposes to smaller fragments, or rearranges to a more stable isomer.



Scheme 1

Results and discussion

We have chosen to describe the theoretical aspects of this project first and then to investigate whether the experimental data are in accord with the theoretical findings.

A: The evidence based on theory

Rearrangements and decompositions of $[CCOCC]^{-\bullet}$

If $[CCOCC]^{-\bullet}$ can be synthesised, will it be an appropriate precursor for neutral CCOCC? In other words, will this anion radical survive the collisional conditions necessary to effect one-electron stripping to form the required neutral? For example, will $[CCOCC]^{-\bullet}$ (i) dissociate to smaller fragments under these conditions, or (ii) rearrange to form a more stable radical anion isomer?

The energies and connectivities of doublet radical anions are shown in Scheme 1. Relative energies are with respect to $[CCCCO]^{-\bullet}$ (0 kJ mol^{-1}). If $[CCOCC]^{-\bullet}$ (**2**$^{-\bullet}$) were to rearrange to a more stable isomer during or following collisional

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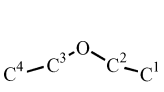
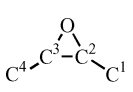
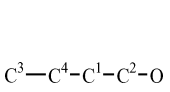
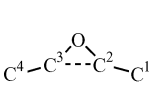
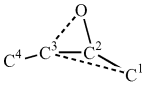
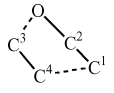
Table 1 Energies and geometries of doublet anions

	 **2**$^{-\bullet}$	 **7**$^{-\bullet}$	 **1**$^{-\bullet}$	 **TS 2**$^{-\bullet}$**/7**$^{-\bullet}$	 **TS 7**$^{-\bullet}$**/1**$^{-\bullet}$	 **TS 2**$^{-\bullet}$**/1**$^{-\bullet}$
State	$^2B_1$	$^2B_2$	$^2\Pi$	$^2B_2$	$^2A'$	$^2A'$
Symmetry	C_{2v}	C_{2v}	$C_{\infty v}$	C_{2v}	C_s	C_s
Energy/E_h	−226.80179	−226.78718	−226.94076	−226.75426	−226.78022	−226.76603
Dipole moment[b]/D	2.52	3.18	4.36	—	—	—
Bond length/Å[b]						
C^1C^2	1.267	1.295	1.263	1.277	1.316	1.294
C^1C^3	—	—	—	—	2.558	—
C^1C^4	—	—	1.337	—	—	2.538
C^2C^3	2.332	1.561	—	1.837	1.454	—
C^3C^4	1.267	1.295	1.281	1.277	1.292	1.317
C^2O	1.324	1.409	1.216	1.370	1.365	1.362
C^3O	1.324	1.409		1.370	1.690	1.447
Bond angle/°[b]						
$C^1C^2C^3$	159.6	149.7	180.0	143.7	134.8	145.5
$C^2C^3C^4$	159.6	149.7	180.0	143.7	170.5	72.7
OC^1C^2	—	—	180.0	—	—	—
OC^2C^3	28.3	56.4	—	47.9	73.6	52.0
$C^1C^2OC^3$	180.0	180.0	—	180.0	180.0	180.0
$C^2OC^3C^4$	180.0	180.0	—	180.0	180.0	0.0

[a] CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory including zero-point energy (B3LYP/6-31G*, scaled by 0.9804).[39] [b] B3LYP/6-31G* level of theory.

activation, possible rearrangement sequences might be **2**$^{-\bullet}$ → **7**$^{-\bullet}$ → **8**$^{-\bullet}$ → **1**$^{-\bullet}$ or **2**$^{-\bullet}$ → **7**$^{-\bullet}$ → **6**$^{-\bullet}$ → **1**$^{-\bullet}$ (see Scheme 1).

We have investigated the potential surface of the doublet $[CCOCC]^{-\bullet}$ system using the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. The results are summarised in Fig. 1, with full details of minima and transition states listed in Table 1. The two most favourable reaction pathways are shown in Fig. 1: both are exothermic by 365 kJ mol^{-1}, but neither occurs precisely by the interconversion pathways suggested above. The first is a stepwise process which proceeds through cyclic intermediate **7**$^{-\bullet}$ over a barrier of 125 kJ mol^{-1}, the second is a synchronous process proceeding through a cyclic transition state 94 kJ mol^{-1} above reactant $[CCOCC]^{-\bullet}$ Rearrangements of negative ions of this type are the exception rather than the rule;[26] those that have been confirmed have barriers ≤55 kJ mol^{-1}.[27] It thus seems likely that $[CCOCC]^{-\bullet}$, once formed, should be stable under the collisional conditions required to convert $[CCOCC]^{-\bullet}$ to CCOCC. The data in Fig. 1 indicate that the majority of $[CCOCC]^{-\bullet}$ species should be stable under collisional conditions. However, if there is minor rearrangement forming $[CCCCO]^{-\bullet}$, the product anions may be energised with an excess energy of 459 kJ mol^{-1} [the energy difference between **TS 2**$^{-\bullet}$**/1**$^{-\bullet}$ and **1**$^{-\bullet}$ (Fig. 1)]. The lowest energy dissociation pathway of $[CCCCO]^{-\bullet}$, namely $[CCCCO]^{-\bullet}$ → $[CCC]^{-\bullet}$ + CO, is endothermic by 151 kJ mol^{-1} (Table 2) at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory.[23] The majority of the $[CCCCO]^{-\bullet}$ product anions formed in this way will therefore decompose in the ion source, others may be collision stabilised and not decompose.

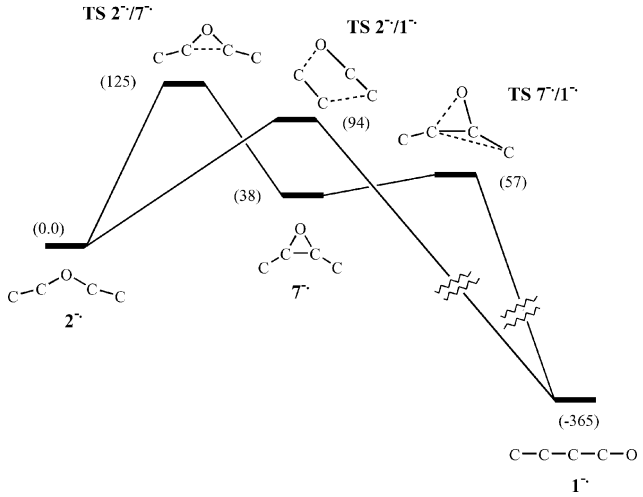


Fig. 1 Rearrangement of $[CCOCC]^{-\bullet}$ to $[CCCCO]^{-\bullet}$. Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Relative energies in kJ mol^{-1}. Structures drawn on the figure indicate bond connectivities but not bond order.

Table 2 Anionic dissociation pathways[a]

$[CCOCC]^{-\bullet}$ → $[CCOC]^{-\bullet}$ + C	510 kJ mol^{-1}
$[CCOCC]^{-\bullet}$ → $[CC]^{-\bullet}$ + CCO	150 kJ mol^{-1}
$[CCCCO]^{-\bullet}$ → $[CCC]^{-\bullet}$ + CO	151 kJ mol^{-1}

[a] CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Energy values were determined from the following theoretically calculated values (in E_h): $[CCOC]^{-\bullet}$ = −188.84277, C = −37.76487, $[CC]^{-\bullet}$ = −75.84224, CCO = −150.90248, $CCC^{-\bullet}$ = −113.81418, CO = −113.06894.

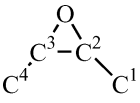
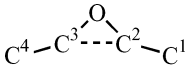
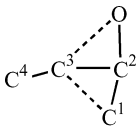
Theoretical calculations indicate that $[CCOCC]^{-\bullet}$ is a suitable precursor to effect one-electron oxidation to form CCOCC. The next question that needs to be answered is whether vertical oxidation of $[CCOCC]^{-\bullet}$ produces a stable, rearranging or decomposing neutral. There are, in principle, singlet and triplet forms of the ten neutral C_4O isomers with structures analogous to those of the anions shown in Scheme 1.† These are also shown in Scheme 1, with a minority of the structures being

† The level of theory used in this study, namely CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d), is the same as that used successfully in previous studies. However, it has been correctly pointed out to us by a reviewer that by using the unrestricted theory [UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31G(d)], and by manually swapping the α HOMO for an α LUMO (orbitals 16 and 17), a singlet diradical state of CCCCO is achievable which is 22 kJ mol^{-1} lower in energy than the closed shell singlet state that we have quoted. This does not change the conclusions made in this paper or any of our previous papers, including our C_4O paper.[23] The data for this open shell state are as follows: state = $^1\Delta$, point group = $C_{\infty v}$, energy in E_h (with zero point correction and scaling) = −226.83035, $C^4C^3C^2C^1O$; OC^1 = 1.175, C^1C^2 = 1.288, C^2C^3 = 1.290, C^3C^4 = 1.313.

unstable at the level of theory used for these calculations. The singlet is the ground state of CCOCC lying 445 kJ mol^{-1} above singlet CCCCO, the global minimum on the potential surface. In contrast, the triplet is the ground state of CCCCO. The singlet and triplet states of CCOCC are 51 kJ mol^{-1} different in energy (the singlet is lower in energy) and have similar geometries best represented by the bent structure C≡C–O–C≡C (COC angles 126.9° and 153.5° for singlet and triplet structures respectively (see Tables 3 and 4). Franck–Condon oxidation of $[CCOCC]^{-\bullet}$ will produce both singlet and triplet CCOCC, and so reaction coordinate profiles of both singlet and triplet CCOCC systems must be considered. Since the singlet and triplet of CCOCC are such high energy species, it seems likely that CCOCC, on formation, might rearrange to a more stable isomer [*e.g.* **7**, **8** or **1** (see Scheme 1)].

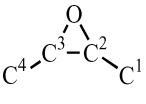
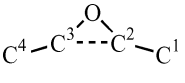
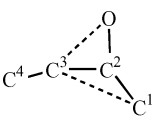
Reaction coordinate diagrams for the lowest energy rearrangement pathways for singlet and triplet CCOCC are summarised in Figs. 2 and 3, with full details of minima and transitions states recorded in Tables 3 and 4 respectively. Both processes are stepwise with maximum barriers of 9 kJ mol^{-1} (singlet) and 16 kJ mol^{-1} (triplet). The processes are strongly exothermic; singlet (−445 kJ mol^{-1}) and triplet (−532 kJ mol^{-1}). The Franck–Condon excess energies (the energy difference between CCOCC and the energy of the neutral CCOCC with the anion geometry) are calculated to be 10 and 35 kJ mol^{-1} for the singlet and triplet respectively. Thus both singlet and triplet CCOCC are formed

Table 3 Energies and geometries of singlet neutrals

					
	^{1}**2**	^{1}**7**	^{1}**1**	**TS ^{1}2/^{1}7**	**TS ^{1}7/^{1}1**
State	$^1A_1$	$^1A_1$	$^1\Sigma$	^1A	$^1A'$
Symmetry	C_{2v}	C_{2v}	$C_{\infty v}$	C_2	C_s
Energy/E_h[a]	−226.65235	−226.67478	−226.82200	−226.64901	−226.65815
Dipole moment[b]/D	1.37	0.98	2.12	—	—
Bond length/Å[b]					
C^1C^2	1.293	1.321	1.290	1.298	1.304
C^1C^3			1.292		1.674
C^2C^3	2.304	1.436		1.949	1.494
C^3C^4	1.293	1.321	1.312	1.298	1.329
C^2O	1.288	1.403	1.176	1.328	1.314
C^3O	1.288	1.403		1.328	1.613
Bond angle/°[b]					
$C^1C^2C^3$	162.6	151.9	180.0	144.0	73.1
$C^2C^3C^4$	162.6	151.9	180.0	144.0	167.7
OC^1C^2			180.0		
OC^2C^3	26.6	59.2		42.8	69.8
$C^1C^2OC^3$	180.0	180.0		121.3	0.0
$C^2OC^3C^4$	180.0	180.0		121.3	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).[39] [b] B3LYP/6-31G* level of theory.

Table 4 Energies and geometries of triplet neutrals

					
	^{3}**2**	^{3}**7**	^{3}**1**	**TS ^{3}2/^{3}7**	**TS ^{3}7/^{3}1**
State	$^3B_1$	$^3A''$	$^3\Sigma$	$^3A''$	$^3A''$
Symmetry	C_{2v}	C_s	$C_{\infty v}$	C_s	C_s
Energy/E_h[a]	−226.63305	−266.63996	−226.83576	−226.63001	−266.62687
Dipole moment[b]/D	0.66	1.37	2.32	—	—
Bond length/Å[b]					
C^1C^2	1.297	1.388	1.288	1.332	1.391
C^1C^3	—	—	1.289	—	2.609
C^2C^3	2.457	1.451		1.701	1.420
C^3C^4	1.297	1.307	1.314	1.296	1.305
C^2O	1.262	1.3400	1.175	1.312	1.305
C^3O	1.262	1.4740		1.384	1.706
Bond angle/°[b]					
$C^1C^2C^3$	173.9	152.2	180.0	150.4	136.2
$C^2C^3C^4$	173.9	155.5	180.0	153.3	170.8
OC^1C^2	—	—	180.0	—	—
OC^2C^3	13.3	61.9	—	52.8	77.4
$C^1C^2OC^3$	180.0	180.0	—	180.0	180.0
$C^2OC^3C^4$	180.0	180.0	—	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).[39] [b] B3LYP/6-31G* level of theory.

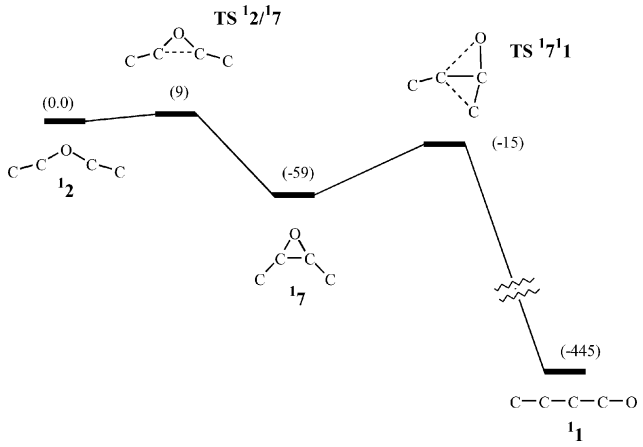


Fig. 2 Rearrangement of singlet CCOCC to singlet CCCCO. Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Relative energies in kJ mol^{-1}. Structures drawn on the figure indicate bond connectivities but not bond order.

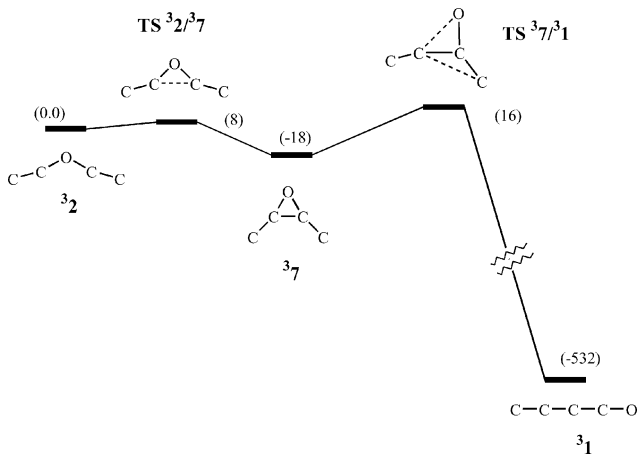


Fig. 3 Rearrangement of triplet CCOCC to triplet CCCCO. Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. Relative energies in kJ mol^{-1}. Structures drawn on the figure indicate bond connectivities but not bond order.

with sufficient excess energy to effect the favoured rearrangement pathways shown in Figs. 2 and 3.

The two rearrangement pathways produce energised CCCCO [singlet 454 kJ mol^{-1} and triplet (−548 kJ mol^{-1})]. The major dissociation pathways of CCCCO have been reported.[23] The lowest energy pathways for both singlet and triplet are CC-CCO → CCC + CO. These processes are endothermic; requiring 19 and 256 kJ mol^{-1} for the singlet and triplet processes. Thus, the rearrangement of the singlet (Fig. 2), should produce the decomposition products CCC and CO almost exclusively. In contrast, the triplet rearrangement should produce some CCCCO neutrals which decompose to CCC and CO, while other CCCCO neutrals will be collision stabilised (in the collision cell) and not decompose.

In summary, the theoretical study suggests that (i) [CCOCC]$^{-\bullet}$ should be a suitable precursor for vertical one-electron oxidation to form CCOCC, (ii) both singlet and triplet CCOCC should rearrange to CCCCO in highly exothermic reactions over minimal barriers, and (iii) the singlet rearrangement should produce energised CCCCO which decomposes to form CCC and CO, while the analogous triplet rearrangement will form some non-decomposing and some decomposing CCCCO species.

B: The evidence based on experimental results

The anion [CCOCC]$^{-\bullet}$ was made in the ion source of the VG ZAB 2HF mass spectrometer by the process shown in eqn (1), a modification[28] of the sequential F^- / S_N2(Si) process first described by Squires.[25] The precise mechanism of this stepwise process is not known (*e.g.* whether it involves reaction first with F^- and then with $F^\bullet$, or whether there are two S_N2(Si) reactions with F^- accompanied by an electron transfer within a reaction intermediate).

$$e + SF_6 + (CH_3)_3Si–C{\equiv}C–O–C{\equiv}C–Si(CH_3)_3 \rightarrow [CCOCC]^{-\bullet} + SF_4 + 2(CH_3)_3SiF \quad (1)$$

The CID mass spectrum of [CCOCC]$^{-\bullet}$ shows a pronounced parent radical anion at *m/z* 64 with a small peak (0.1% relative abundance) due to loss of CO. The latter peak suggests the presence of a minor rearranged isomer which can readily lose CO [*e.g.* isomers **1**$^-$,**6**$^-$ or **8**$^-$ are possibilities (Scheme 1)]. These data are in accord with the molecular modelling study which suggests that the majority of energised [CCOCC]$^{-\bullet}$ anion radicals retain their bond connectivity, with the possibility of minor rearrangement to both stable and decomposing [CCCCO]$^{-\bullet}$.

The charge reversal spectrum of [CCOCC]$^{-\bullet}$ [$^-$CR$^+$, synchronous splitting of two electrons from the anion radical to give the corresponding cation radical (both stable and decomposing)] is shown in Fig. 4. This spectrum is, within experimental error, identical with the $^-$CR$^+$ spectrum of [CCCCO]$^{-\bullet}$,[23] suggesting that the first formed [CCOCC]$^{+\bullet}$ rearranges completely to [CCCCO]$^{+\bullet}$. The $^-$NR$^+$ spectrum of [CCOCC]$^{-\bullet}$ (one electron oxidation of [CCOCC]$^{-\bullet}$ to neutrals in the first collision cell, then a second one-electron oxidation to form cations in the second collision cell) is very noisy and weak and not appropriate to record as a figure. Indeed, some of the minor peaks needed to be scanned manually in order to confirm their presence. The $^-$NR$^+$ spectrum is as follows (error ± 10% in the abundance of any peak) [*m/z* (loss or formation) relative abundance in%]: 64 (recovery signal) 62; 52 (–C) 7; 48 (–O) 5; 40 (–CC) 2; 36 (–CO) 100; 28 ($CO^{+\cdot}$) 8; 24 ($CC^{+\cdot}$) 5. The $^-$NR$^+$ spectrum shows a number of peaks formed from fragment cations that are the same as those observed in the $^-$CR$^+$ spectrum of [CCOCC]$^{-\bullet}$ (Fig. 4): these data do not tell us whether it is the neutral or the cation which is rearranging. However, there are two peaks in the $^-$NR$^+$ spectrum that are significantly more abundant than those of the $^-$CR$^+$ spectrum. These are the base peak in the $^-$NR$^+$ spectrum [$(CCC)^{+\bullet}$, formed by loss of CO), and the peak at *m/z* 28 $(CO)^{+\bullet}$]. The additional intensities of these peaks in the $^-$NR$^+$ spectrum must be due to a neutral which is able to decompose to CCC and CO, followed by ionisation of these species to $[CCC]^{+\bullet}$ and $[CO^{+\bullet}]$ respectively. This result by itself is does not prove that the rearranged neutral is CCCCO since there are other

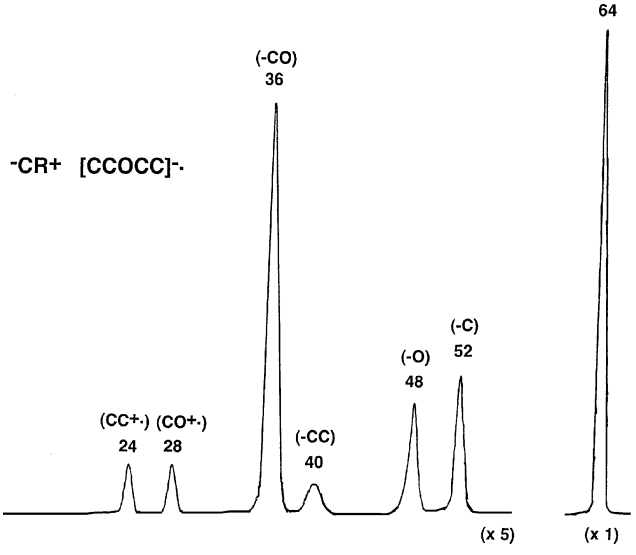


Fig. 4 $^-$CR$^+$ mass spectrum of [CCOCC]$^{-\bullet}$. VG ZAB 2HF mass spectrometer. For operating conditions see the Experimental section.

isomers shown in Scheme 1 which may lose CO (*e.g.* **4** and **8**). However, the experimental data (and findings) outlined above (i) do indicate rearrangement of CCOCC to a neutral species which decomposes to form CCC and CO, and (ii) are consistent with the predictions of the theoretical study.

In conclusion, we propose from a consideration of both experimental and theoretical results that Franck–Condon one-electron vertical oxidation of $[CCOCC]^{-\bullet}$ gives a mixture of energised singlet and triplet CCOCC neutrals which rearrange over small barriers to produce singlet and triplet CCCCO in exothermic reactions. Some of the CCCCO neutrals formed by rearrangement are stable for the microsecond duration of the NR experiment (mainly the triplet), while others (mainly the singlet) are energised and decompose to form CCC and CO.

Experimental

A Mass spectrometric methods

For a detailed description of the instrument used, see ref. 28. 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 $[CCOCC]^{-\bullet}$ was formed in the chemical ionisation source by the process shown in eqn. 1.

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 [SF_6 (for F^-)] was introduced through a gas inlet into the ion source, to give 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 (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.[29] Product anion peaks resulting from CID processes were recorded by scanning E. The charge reversal ($^-CR^+$) spectrum[30,31] was recorded using single collision conditions in collision cell 1 (O_2, 80% transmission of main beam). Neutralisation of anions ($^-NR^+$)[32–34] was effected by collisional electron detachment using O_2 (at 80% transmittance of the main beam) as the collision gas in both collision cells.

B Synthetic procedures

TMSC≡C–O–C≡CTMS was prepared by a reported procedure.[35]

C Theoretical methods

Geometry optimisations were carried out with the Becke 3LYP method[36,37] using the 6-31G* basis set within the GAUSSIAN 98 suite of programs.[38] 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.[39] We have previously reported the success of the B3LYP method in predicting geometries of unsaturated chain structures, and that this method produces optimized structures, at low computational cost, that compare well with higher level calculations.[40] More accurate energies for the B3LYP geometries were determined using the coupled cluster CCSD(T) method[41] using the Dunning aug-cc-pVDZ basis set.[42,43] All calculations were carried out on the Alpha Server at the Australian Partnership for Advanced Computing (APAC) National Facility (Canberra).

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References

1 H. Olofsson, *Molecules in the Stellar Environment, Lecture Notes in Physics*, ed. O. G. Jorgenson, Springer, Heidelberg, 1994, pp. 114–133, and refs. cited therein.
2 P. F. Bernath, K. H. Hinkleand and J. J. Keady, *Science*, 1989, **244**, 562; K. H. Hinkle, *Molecules in the Stellar Environment, Lecture Notes in Physics*, ed. O. G. Jorgenson, Springer, Heidelberg, 1994, pp. 99-114, and refs. cited therein.
3 S. J. Blanksby and J. H. Bowie, *Mass Spectrom. Rev.*, 1999, **18**, 81.
4 For a list of stellar molecules so far identified see, H. A. Wootten, http://www.cv.nrao.edu/~awootten/allmols.html.
5 M. Ohishi, H. Suzuki, S. Ishikawa, C. Yamada, H. Kanamori, W. M. Irvine, R. D. Brown, P. D. Godfrey and N. Kaifu, *Astrophys. J.*, 1991, **380**, L39.
6 H. E. Matthews, W. M. Irvine, P. Friberg, R. D. Brown and P. D. Godfrey, *Nature*, 1984, **310**, 125.
7 B. E. Turner, *Chemistry and Spectroscopy of Interstellar Molecules.* ed. D. K. Bohme, University of Tokyo Press, 1992, p. 75.
8 S. Dua, S. J. Blanksby and J. H. Bowie, *Int. J. Mass Spectrom.*, 2000, **195/196**, 45.
9 R. D. Brown, F. W. Eastwood, P. S. Elmes and P. D. Godfrey, *J. Am. Chem. Soc.*, 1983, **105**, 6496.
10 R. D. Brown, D. A. McNaughton and K. G. Dyall, *Chem. Physics*, 1988, **119**, 89; R. G. A. R. Maclagan and P. Sudkeaw, *J. Chem. Soc. Faraday Trans.*, 1993, **89**, 3325.
11 M. Moazzen-Ahmalsi and F. Zerbetto, *J. Chem. Phys.*, 1995, **103**, 6343.
12 P. Botschwina, P. Flgge and P. Sebald, *J. Phys. Chem.*, 1995, **99**, 9755.
13 T. Ogata, Y. Ohshima and Y. Endo Y, *J. Am. Chem. Soc.*, 1995, **117**, 3593.
14 Y. Ohshima, Y. Endo and T. Ogata, *J. Chem. Phys.*, 1995, **102**, 1493.
15 J. M. Oakes and G. B. Ellison, *Tetrahedron*, 1986, **42**, 6263.
16 R. D. Brown, P. D. Godfrey, P. S. Elmes, M. Podler and L. M. Tack, *J. Am. Chem. Soc.*, 1985, **107**, 4112.
17 D. W. Ewing, *J. Am. Chem. Soc.*, 1989, **111**, 8809.
18 H. Kannari, K. Aoki, K. Hashimoto and S. Ikuta, *Chem. Phys. Lett.*, 1994, **222**, 313.
19 S. T. Brown, J. C. Rienstra-Kiracofe and H. F. Schaefer, *J. Phys. Chem.*, 1999, **103**, 4065.
20 J. C. Rienstra-Kiracofe, G. B. Ellison, B. C. Hoffman and H. F. Schaefer, *J. Phys. Chem.*, 2000, **104**, 2273.
21 E. Riaplov, M. Wyss, N. M. Lakin and J. P. Maier, *J. Phys. Chem.*, 2001, **105**, 4894.
22 J. C. Rienstra-Kiracofe, G. S. Tschumper, H. F. Schaefer, S. Nandi and B. Ellison, *Chem. Rev.*, 2002, **102**, 231.
23 M. Fitzgerald, A. M. McAnoy, J. H. Bowie, D. Schröder and H. Schwarz, *Org. Biomol. Chem.*, 2005, **3**, 901.
24 C. H. DePuy, V. M. Bierbaum, L. A. Flippin, J. J. Grabowski, G. K. King, R. J. Schmitt and S. A. Sullivan, *J. Am. Chem. Soc.*, 1980, **102**, 5012.
25 P. G. Wenthold, J. Hu and R. R. Squires, *J. Am. Chem. Soc.*, 1994, **116**, 6961.
26 S. Dua, S. J. Blanksby, S. Peppe, A. M. McAnoy and J. H. Bowie, *Curr. Org. Chem.*, 2003, **7**, 1545.
27 S. Dua and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 2001, 827.
28 S. J. Blanksby, D. Schröder, S. Dua, J. H. Bowie and H. Schwarz, *J. Am. Chem. Soc.*, 2000, **122**, 7105.
29 J. L. Holmes, *Org. Mass Spectrom.*, 1985, **20**, 69.
30 J. H. Bowie and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **97**, 2959; J. E. Szulejko, J. H. Bowie, I. Howe and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **13**, 76.
31 M. M. Bursey, *Mass Spectrom. Rev.*, 1990, **9**, 555.
32 C. Wesdemiotis and F. W. McLafferty, *Chem. Rev.*, 1987, **87**, 485.
33 D. V. Zagorevskii and J. L. Holmes, *Mass Spectrom. Rev*, 1994, **13**, 133; N. Goldberg and H. Schwarz, *Acc. Chem. Res.*, 1994, **27**, 347.
34 For NR nomenclature, seeC. A. Schalley, G. Hornung, D. Schröder and H. Schwarz, *Int. J. Mass Spectrom. Ion. Processes*, 1998, **172**, 181; D. V. Zagorevskii and J. L. Holmes, *Mass Spectrom. Rev.*, 1999, **18**, 87.

35 I. H. Ooi and R. H. Smithers, *J. Org. Chem.*, 1989, **54**, 1479.
36 A. D. Becke, *J. Chem. Phys*, 1993, **98**, 5648.
37 P. J. Stevens, F. J. Devlin, C. F. Chablowski and M. J. Frische, *J. Phys. Chem.*, 1994, **98**, 11623.
38 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, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-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.
39 M. W. Wong, *Chem. Phys. Lett*., 1996, **256**, 391.
40 S. J. Blanksby, S. Dua and J. H. Bowie, *J. Phys. Chem.*, 1999, **103**, 5161.
41 M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.*, 1994, **227**, 321, and references cited therein.
42 T. H. Dunning, *J. Chem. Phys*, 1989, **90**, 1007; D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358.
43 T. H. Dunning, K. A. Peterson and D. E. Woon, in *Encyclopedia of Computational Chemistry*, ed. P. v. R. Schleyer, Wiley, Chichester, 1998.