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Gas phase generation of the neutrals H_2CCCCO, HCCCCDO and CCCHCHO from anionic precursors. Rearrangements of HCCCCDO and CCCHCHO. A joint experimental and theoretical study

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The reaction between $O^{-\bullet}$ and MeO–CH_2–C≡C–CDO in the ion source of a VG ZAB 2HF mass spectrometer gives a number of product anions including $[H_2CCCCO]^{-\bullet}$ and $[HCCCCDO]^{-\bullet}$ (in the ratio 1 : 5). Neutralisation–reionisation ($^-NR^+$) of $[H_2CCCCO]^{-\bullet}$ results in the sequential two-electron vertical oxidation $[H_2CCCCO]^{-\bullet} \longrightarrow H_2CCCCO \longrightarrow [H_2CCCCO]^{+\bullet}$. Singlet H_2CCCCO lies 158 kJ mol^{-1} below the triplet [at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory]. The majority of neutrals H_2CCCCO are stable for the microsecond duration of the NR experiment, but some are energised and decompose to give H_2CCC and CO. A similar $^-NR^+$ experiment with $[HCCCCDO]^{-\bullet}$ yields neutrals HCCCCDO, some of which are excited and rearrange. Calculations show that it is the singlet form of HCCCCHO which rearranges (the singlet lies 36 kJ mol^{-1} above the ground state triplet): the rearrangement occurs by the sequencial H transfer process, HCCCCHO $\longrightarrow$ HCC(CH)CO $\longleftarrow$ H_2CCCCO. Neutral HCCCCHO needs an excess energy of only 43 kJ mol^{-1} to effect this reaction, which is exothermic by 230 kJ mol^{-1}. Both HCC(CH)CO and H_2CCCCO formed in this way should have sufficient excess energy to cause some loss of CO. The anions $[CC(CH)CHO]^{-\bullet}$ and $[CC(CD)CHO]^{-\bullet}$ are formed in the ion source of the mass spectrometer by the reactions of HO^- with Me_3SiC≡C–CH=CHOMe and Me_3SiC≡C–CD=CHOMe respectively. $^-NR^+$ of these anions indicate that energised forms of CC(CH)CHO and CC(CD)CHO may rearrange to isomer(s) which decompose by loss of CO. Singlet CC(CH)CHO rearranges to HCC(CH)CO and H_2CCCCO, both of which are energised and fragment by loss of CO.

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_nH (n = 2–8) and C_nH_2 (n = 2–4 and 6) molecules.[1–6] In contrast, there has been only limited detection of polycarbon monoxides. The linear species C_2O and C_3O [together with the associated propynal (HC≡C–CHO)] have been detected towards the dark molecular cloud TMC-1,[7,8] and the photoelectron spectra of these species have also been determined.[9]

Few cumulenes containing four carbon atoms have been detected in either interstellar dust clouds or circumstellar envelopes. The linear and rhombic isomers of C_4 have been described,[10] but these symmetrical species have not, as yet, been detected as stellar molecules. Neither have the cumulene oxides CCCCO or HCCCCO, although spectroscopic and/or structural details of CCCCO[9,11–15] and HCCCCO[16,17] have been reported. The only C_4 cumulene so far be detected in the stellar environment is HCCCC.[5,18] Preliminary measurements suggest that C_5O may be present in the stellar medium but this has yet to be confirmed.[19] Linear C_5O has been synthesised from an anionic precursor.[20] A number of theoretical studies have been devoted to polycarbon monoxides.[14,21–24]

We have previously made HC_nO and $C_{n-1}CHO$ isomers (n = 3–5) by neutralisation of ionic precursors,[25–27] and have shown that energised $C_{n-1}CHO$ species rearrange to the more stable HC_nO isomers under the conditions of the neutralisation process. A combination of ^2H and ^{13}C labelling together with *ab initio* calculations show that the rearrangement processes occur by successive H transfers along the carbon backbone without any change in the carbon–oxygen backbone of these molecules.

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The present investigation involves the study of three neutral isomers C_4H_2O including H_2CCCCO. Butatrienone (H_2CCCCO) has been made by flash pyrolysis of suitable anhydrides[28–30] and its structure has been confirmed by microwave[28] and infrared spectroscopy.[29] This molecule has also been studied by high level theoretical calculations[30–36] and there has been significant debate as to whether it is linear or bent. The most recent study[36] suggests that the linear and bent structures differ in energy by only 0.5 kJ mol^{-1}.

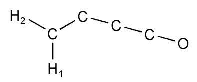
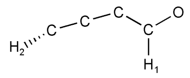
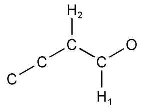
The aims of the present investigation are: (i) to make the potential stellar neutrals H_2CCCCO, HCCCCHO and CCCHCHO (or ^2H labelled analogues as appropriate) from anion precursors in the gas phase, and (ii) to ascertain whether these neutrals rearrange during the microsecond timeframe of the $^-NR^+$ experiment. For example, does HCCCCHO rearrange to H_2CCCCO by a similar process to that observed previously for the rearrangement of CCCCHO to HCCCCO, and if so, can a similar rearrangement occur with CCCHCHO?

Results and discussion

1 H_2CCCCO and HCCCCDO

The reaction of a molecule containing a function XCH_2Y (where X and Y are electronegative substituents) with $O^{-\bullet}$ may lead to the formation of products $[XCY]^{-\bullet}$ and H_2O.[37] However $O^{-\bullet}$ may also act as a gas phase base leading to the formation of $[XCHY]^-$. In a previous study we attempted to use the reaction between $MeOCH_2C$≡C–CDO and $O^{-\bullet}$ to form $[CCCCDO]^-$ (m/z 66) as shown in eqn. 1.[26] This reaction does not occur, instead, $[HCCCCO]^-$ (m/z 65) is formed as shown in eqn. 2. There is a peak at m/z 66 but this is shown to correspond to $[H_2CCCCO]^{-\bullet}$ [as shown by its spectra (see below)], formed by the process shown in eqn. 3. The two peaks at m/z 65 and 66

Table 1 Geometries and energies of anions[a]

			
State	$^2A'$		$^2A''$
Symmetry	*Cs*	*C*1	*Cs*
Energy/Hartrees	−228.15920	−228.12936	−228.15357
Rel. energy/kJ mol^{-1}	0	78	15
Dipole moment/debye	0.94	1.55	4.02
Bond length/Å or angle/°			
C1C2[b]	1.267	1.388	1.431
C2C3	1.329	1.298	1.379
C3C4	1.335	1.291	1.274
C1O	1.225	1.251	1.245
C1H1		1.129	1.116
C4H1	1.095		
C2H2			1.095
C4H2	1.102	1.082	
C1C2C3	170.7	158.3	123.9
C2C3C4	154.1	172.4	179.9
OC1C2	177.1	130.3	126.3
H1C1C2		111.9	113.9
H1C4C3	122.3		
H2C2C3			121.0
H2C4C3	123.6	131.8	
C1C2C3C4	180.0	120.6	0.0
OC1C2C3	180.0	173.3	180.0
H1C1C2C3		−6.7	0.0
H1C4C3C2	180.0		
H2C2C3C4			180.0
H2C4C3C2	0.0	155.4	

[a] Geometries B3LYP/6-31G(d); energies CCSD(T)/aug-cc-pvdz//B3LYP/6-31G(d), corrected for zero point energy, and scaled by 0.9804.[38] [b] Carbons numbered C_1 to C_4. C_1 is the carbon adjacent to O.

co-occur with *m*/*z* 67, which corresponds to $[HCCCCDO]^{-\bullet}$ (eqn. 4). The ratio of the product peaks for the reactions shown in eqns 2–4 (*m*/*z* 65 : 66 : 67) is 1 : 1 : 5.

$$MeO–CH_2–C{\equiv}C–CDO + O^{-\bullet} \rightarrow [CCCCDO]^- + H_2O + MeO^\bullet \tag{1}$$

$$\rightarrow [HCCCCO]^- + HO^\bullet + (MeO^\bullet + D^\bullet) \tag{2}$$

$$\rightarrow [H_2CCCCO]^{-\bullet} + DO^\bullet + MeO^\bullet \tag{3}$$

$$\rightarrow [HCCCCDO]^{-\bullet} + HO^\bullet + MeO^\bullet \tag{4}$$

The doublet anion radicals $[H_2CCCCO]^{-\bullet}$ and $[HCCCCDO]^{-\bullet}$ are stable species (Table 1), and as such may be suitable precursors for neutrals H_2CCCCO and HCCCCDO. The collision induced mass spectra (MS/MS) of the two radical anions are shown in Fig. 1. The two spectra are different. The mass spectrum of $[H_2CCCCO]^{-\bullet}$ (Fig. 1A), shows competitive losses of $H^\bullet$ and CO, losses consistent with the structure of the parent radical anion. In contrast, the mass spectrum (Fig. 1B) of $[HCCCCDO]^{-\bullet}$ shows loss of $D^\bullet$, $HC^\bullet$, CO and $CDO^\bullet$ The losses of CO observed in the two spectra occur by different mechanisms, since the loss of CO in Fig. 1A gives a Gaussian peak, while the corresponding peak in Fig. 1B is wider and flat-topped. The loss of CO from $[HCCCCDO]^{-\bullet}$ can be rationalised by D^- donation from the ^-CDO portion of the ion complex shown in eqn. 5, with the structure of the product anion $[C_3HD]^{-\bullet}$ not determined. We conclude that the two radical anions do not rearrange under the conditions required to effect one-electron vertical oxidation to the two required neutrals.

$$[HCCCCDO]^{-\bullet} \rightarrow [(HCCC)\ ^-CDO] \rightarrow [C_3HD]^{-\bullet} + CO \tag{5}$$

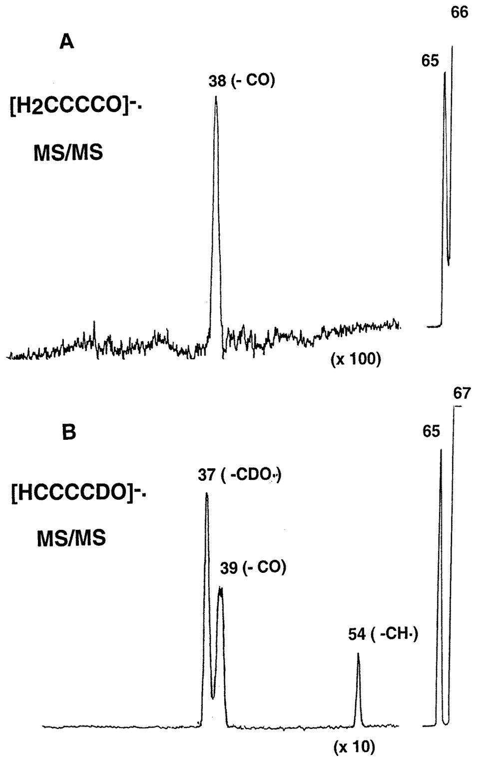


Fig. 1 Collision induced negative ion mass spectra (MS/MS) of (**A**), $[H_2CCCCO]^{-\bullet}$ and (**B**) $[HCCCCDO]^{-\bullet}$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental section.

The charge reversal ($^-CR^+$) and neutralisation–reionisation ($^-NR^+$) mass spectra of $[H_2CCCCO]^{-\bullet}$ and $[HCCCCDO]^{-\bullet}$ are reproduced in Figs 2 and 3 respectively. The $^-CR^+$ spectrum shown in Fig. 2A confirms that the parent radical anion is

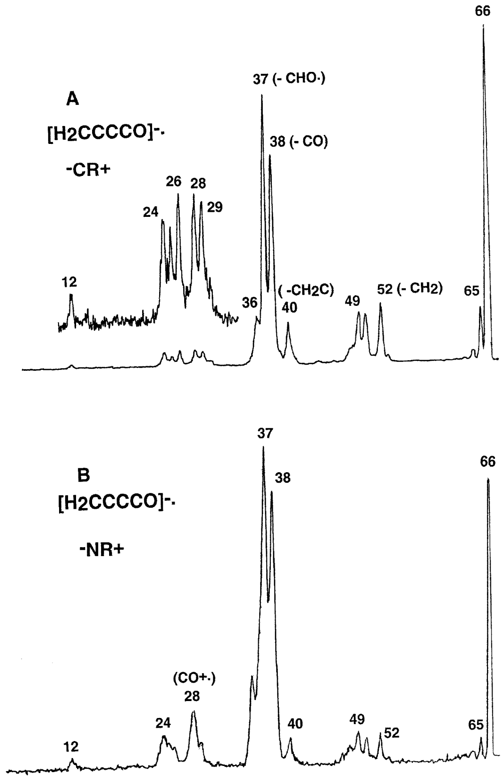


Fig. 2 (**A**) Charge reversal ($^-$CR$^+$) mass spectrum, and (**B**) neutralisation–reionisation mass spectrum of $[H_2CCCCO]^{-\bullet}$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental section.

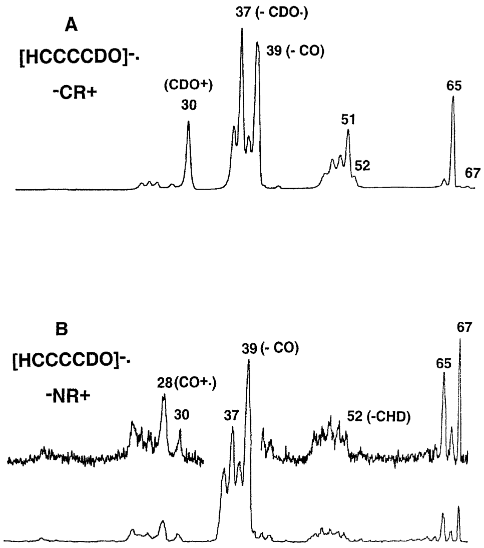


Fig. 3 (**A**) Charge reversal ($^-$CR$^+$) mass spectrum, and (**B**) neutralisation–reionisation ($^-$NR$^+$) mass spectrum of $[HCCCCDO]^{-\bullet}$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental Section.

$[H_2CCCCO]^{-\bullet}$ rather than the isobaric species $[CCCCDO]^-$. Major peaks in the $^-$CR$^+$ spectrum, are due to the competitive losses of H, CH_2, O, CH_2C, CO and (CO + H) from the parent radical cation (the base peak in the spectrum). The $^-$NR$^+$ spectrum (Fig. 2B) is similar to the $^-$CR$^+$ spectrum, except that there is a larger peak at *m*/*z* 28 ($CO^{+\bullet}$) in the $^-$NR$^+$ spectrum. Neither the $^-$CR$^+$ nor $^-$NR$^+$ spectrum gives any indication of the operation of rearrangement processes. We conclude from these data that the sequencial two-electron oxidation occurs without any detectable rearrangement of the backbone of the radical anion, neutral or radical cation, *i.e.* $[H_2CCCCO]^{-\bullet} \longrightarrow H_2CCCCO \longrightarrow [H_2CCCCO]^{+\bullet}$. The pronounced peak due to the charged parent in the $^-$NR$^+$ spectrum indicates that some of the neutral carbenes H_2CCCCO are stable for the microsecond timeframe of the NR experiment. The enhanced abundance of the peak at *m*/*z* 28 ($CO^{+\bullet}$) in the $^-$NR$^+$ spectrum indicates that some of the H_2CCCCO neutrals are energised and fragment to give H_2CCC and CO. This process is endothermic by 173 kJ mol^{-1} for singlet H_2CCCCO (see Table 2).

Table 2 Decomposition pathways of neutrals

Singlets	Energy/kJ mol^{-1}
$HCCCCHO \longrightarrow CHO^\bullet + C_3H^\bullet$	262
$HCC(CH)CO \longrightarrow HCCCH + CO$	245
$H_2CCCCO \longrightarrow H_2CCC + CO$	173
$CC(CH)CHO \longrightarrow HCCC. + CHO$	298
Triplets	
$HCCCCHO \longrightarrow HCCC. + CHO$	296
$HCC(CH)CO \longrightarrow HCCCH + CO$	73
$H_2CCCCO \longrightarrow H_2CCC + CO$	15

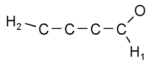
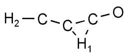
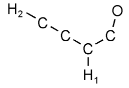
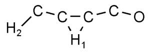
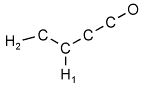
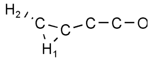
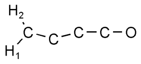
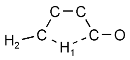
The $^-$CR$^+$ and $^-$NR$^+$ spectra of $[HCCCCDO]^{-\bullet}$ are shown in Figs 3A and 3B respectively. The $^-$CR$^+$ spectrum results from synchronous two-electron vertical conversion of the anion radical to give, at least initially, radical cations corresponding to $[HCCCCDO]^{+\bullet}$, some of which will be energised and either decompose or perhaps rearrange. The $^-$CR$^+$ spectrum shows a very small peak corresponding to the parent cation radical, and a major loss of $D^\bullet$ (to give *m*/*z* 65), consistent with the characteristic α cleavage of a CDO group in the positive ion mode. There are also pronounced peaks at *m*/*z* 37 (HC_3^+) and *m*/*z* 30 (^+CDO), consistent with a system with HCCCCDO connectivity. However, the peaks at *m*/*z* 52 (−CHD) and *m*/*z* 39 (−CO) in this spectrum must come from rearranged species, perhaps $[HDCCCCO]^{+\bullet}$. Thus the $^-$CR$^+$ spectrum of $[CHCCCDO]^{-\bullet}$ is composite: the major component is $[HCCCCDO]^{+\bullet}$ with the minor component possibly $[CHDCCCO]^{+\bullet}$.

The $^-$NR$^+$ spectrum of $[HCCCCDO]^{-\bullet}$ is different from the $^-$CR$^+$ spectrum in the following ways. It shows some peaks which are more abundant than those in the $^-$CR$^+$ spectrum; namely, *m*/*z* 67 (the parent cation radical), 52 (−CHD) and 39 (−CO). Further, the characteristic peak at *m*/*z* 30 (CDO^+) noted in the $^-$CR$^+$ spectrum is only minor in the $^-$NR$^+$ spectrum. This gives a clear indication that the decompositions of $[HCCCCDO]^{+\bullet}$ are minor in the $^-$NR$^+$ spectrum which in turn means that energised neutrals HCCCCDO are undergoing significant rearrangement on the NR time scale, possibly to HDCCCCO.

We have carried out calculations of the rearrangement reaction coordinates of HCCCCHO on the singlet and triplet C_4H_2O potential surfaces at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory using Gaussian 98. All of the stable neutrals on this surface have singlet and triplet forms. Data are contained in Tables 3 and 4. The singlet is the ground state of H_2CCCCO (by 158 kJ mol^{-1}) and may be represented by the linear cumulene oxide structure $H_2C{=}C{=}C{=}C{=}O$ (*cf.* refs 30–35, and see Introduction). The singlet neutral is calculated to have a dipole moment of 2.15 Debye, and an adiabatic electron affinity of 0.82 eV. In contrast, the triplet is the ground state of HCCCCHO (by 36 kJ mol^{-1}), and has a structure best represented as $H^\bullet C{=}C{=}C^\bullet{-}CH{=}O$ (dipole moment 3.11 Debye; adiabatic electron affinity 2.03 eV). Both singlet and triplet states of H_2CCCCO are lower in energy than the corresponding states of HCCCCHO (by 231 and 38 kJ mol^{-1} respectively).

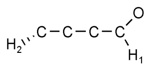
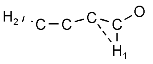
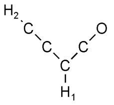
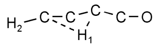
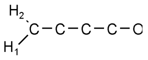
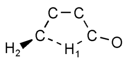
The Franck–Condon neutralisation process may impart some excess energy to the neutral. This may be calculated as the difference in energy between the stable neutral and that neutral (on the neutral potential surface) which has the geometry of the precursor radical anion. These data are contained in Table 5.

Table 3 Geometries and energies of triplet species[a]

								
State	3A″		3A″	3A″	3A″		3A″	3A″
Symmetry	*Cs*	*C*1	*Cs*	*Cs*	*Cs*	*C*1	*Cs*	*Cs*
Energy /Hartrees	−228.05467	−227.95995	−228.07137	−227.96721	−228.04726	−227.97777	−228.06907	−227.96682
Rel. energy /kJ mol^{-1}	38	287	−6	267	57	240	0	267
Dipole/debye	3.11		2.95		3.39		2.78	
Adiabatic electr. affinity/eV	2.03						2.45	
Bond length/Å or angle/°								
C1C2[b]	1.422	1.323	1.467	1.337	1.290	1.280	1.292	1.472
C2C3	1.282	1.308	1.380	1.331	1.392	1.343	1.307	1.336
C3C4	1.269	1.307	1.225	1.303	1.356	1.343	1.362	1.332
C1O	1.229	1.181	1.198	1.189	1.184	1.186	1.187	1.176
C1H1	1.107	1.507						1.502
C2H1		1.373	1.086	1.406				
C3H1				1.358	1.098	1.283		
C4H1						1.364	1.088	1.398
C4H2	1.069	1.091	1.067	1.081	1.084	1.099	1.094	1.083
C1C2C3	177.7	160.2	122.5	157.4	147.8	162.0	164.4	118.5
C2C3C4	176.4	170.4	178.4	164.8	124.4	143.2	143.7	110.5
OC1C2	123.4	175.6	128.7	153.8	170.5	175.6	173.4	138.6
H1C1C2	115.5	57.6	120.1					
H1C2C3				59.4				
H1C3C4					117.6	62.5		
H1C4C3							121.4	102.0
H2C4C3	161.1	133.0	179.4	131.4	135.3	136.1	122.3	141.9
C1C2C3C4	180.0	−158.7	0.0	0.0	0.0	135.3	180.0	0.0
OC1C2C3	0.0	−36.8	0.0	180.0	180.0	−179.0	180.0	180.0
H1C1C2C3	180.0	172.9						
H1C2C3C4			180.0	180.0				
H1C3C2C1					180.0	33.5		
H1C4C3C2							180.0	0.0
H2C4C3C2	180.0	−6.9	0.0	180.0	180.0	8.7	0.0	180.0

[a] Geometries, B3LYP/6-31G(d); energies CCSD(T)/aug-cc-pvdz//B3LYP/6-31G(d) including zero point energy correction, and scaled by 0.9804.[29] [b] Carbons are numbered 1–4. C1 is adjacent to O.

Table 4 Geometries and energies of singlet species[a]

						
State			$^1A'$		$^1A1$	
Symmetry	*C*1	*C*1	*Cs*	*C*1	*C*2*V*	*C*1
Energy/Hartrees	−228.04114	−228.03999	−228.13682	−228.02479	−228.12917	−227.99158
Relative Energy/kJ mol $^{-1}$	231	234	−20	274	0	361
Dipole/debye	3.22		0.90		2.15	
Adiabatic Elec. Affinity/eV	2.40				0.82	
Bond length/Å or angle/°						
C1C2[b]	1.409	1.373	1.329	1.280	1.282	1.533
C2C3	1.279	1.329	1.418	1.373	1.279	1.334
C3C4	1.291	1.240	1.210	1.254	1.312	1.339
C1O	1.229	1.214	1.167	1.184	1.177	1.175
C1H1	1.109	1.153				1.403
C2H1		1.850	1.088	1.595		
C4H1				1.971	1.087	1.464
C4H2	1.084	1.069	1.066	1.067	1.087	1.093
C1C2C3	159.4	142.6	122.0	151.9	180.0	112.1
C2C3C4	168.9	171.1	178.9	172.2	180.0	104.9
OC1C2	121.3	144.3	179.3	174.2	180.0	135.9
H1C1C2	115.4	93.7				90.0
H1C2C3			121.6	45.3		
H1C4C3					121.1	
H2C4C3	129.4	159.0	179.5	164.6	121.1	126.6
C1C2C3C4	−176.2	−173.5	180.0	−162.2		42.3
OC1C2C3	80.8	−118.4	180.0	−172.8		147.8
H1C1C2C3	−101.3	70.0	0.0			−29.1
H1C2C3C4				152.0		
H2C4C3C2	−174.1	−160.2	180.0	−162.1		112.0

[a] Geometries B3LYP/6-31G(d); energies CCSD(T)/aug-cc-pvdz//B3LYP/6-31G(d) including zero point energy correction, scaled by 0.9804.[29] [b] Carbons are numbered C1 to C4. C1 is adjacent to O.

Singlet and triplet H_2CCCCO are formed with Franck–Condon excess energies of 30 and 12 kJ mol^{-1} during the one-electron vertical oxidation of doublet $[H_2CCCCO]^{-\bullet}$. The corresponding Franck–Condon excess energies of triplet and singlet HCCCCHO are 25 and 16 kJ mol^{-1} respectively.

Two possible isomerisation processes of triplet HCCCCHO are shown in Fig. 4. Route **A** shows a three stage 1,2-H rearrangement pathway, and route **B**, a concerted 1,4-H transfer process. Both routes have steps which require the precursor neutral HCCCCHO to have more than 250 kJ mol^{-1} of excess energy; and are unlikely to occur under the conditions of an $^-NR^+$ experiment. However the triplet ground state and singlet HCCCCHO are only 36 kJ mol^{-1} different in energy and both may be formed from the precursor $[HCCCCHO]^{-\bullet}$. In addition, because the singlet and triplet neutrals are so close in energy, the cross over point between the two potential surfaces may be accessible. Thus we must consider rearrangements occurring from the singlet state of HCCCCHO.

The reaction coordinate profiles for the isomerisation of singlet HCCCCHO are shown in Fig. 5. Two pathways are shown. The first, the stepwise pathway **C**, is initiated by a facile 1,2-H transfer, followed by a 2,4-H transfer. The overall process is strongly exothermic, but requires the starting material to have an an excess energy of ≥43 kJ mol^{-1}. Singlet HCCCCHO has an excess Franck–Condon energy of 16 kJ mol^{-1} (see Table 5). This is sufficient to effect conversion of HCCCCHO to HCC(CH)CO, but not HCC(CH)CO to H_2CCCCO. The small amount of extra excess energy required for the second step may be provided by collision of the neutral with collision gas during or subsequent to the neutralisation process.[26] The singlets HCC(CH)CO and H_2CCCCO are formed with excess energies of 254 and 294 kJ mol^{-1} (see Fig. 5), sufficient to cause decomposition by loss of CO in both cases (see Table 2).

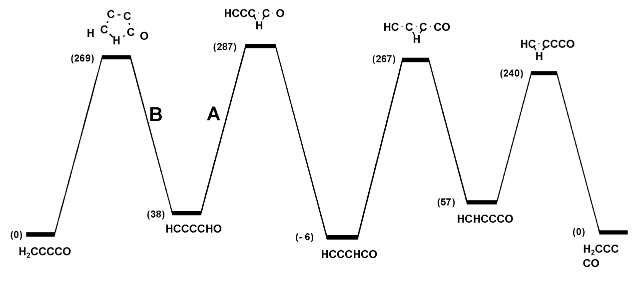


Fig. 4 Reaction coordinates of (**A**), stepwise and, (**B**) concerted rearrangement of triplet HCCCCHO to triplet H_2CCCCO. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6- 31G(d) level of theory. Relative energies in kJ mol^{-1}. The structures in this figure show bond connectivities only. For full details of geometries and energies of all species see Table 3.

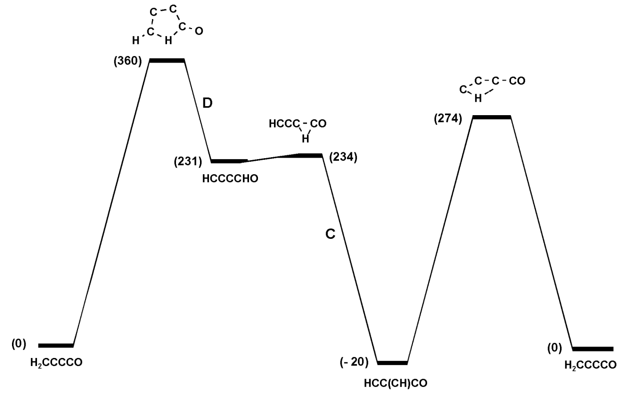


Fig. 5 Reaction coordinates of (**C**), stepwise and, (**D**) concerted rearrangement of singlet HCCCCHO to singlet H_2CCCCO. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kJ mol^{-1}. The structures in this figure show bond connectivities only. For full details of geometries and energies of all species see Table 4.

The concerted 1,4-H rearrangement process (**D**) has a barrier of some 167 kJ mol^{-1} and is unfavourable in comparison to stepwise process **C**.

Table 5 Franck–Condon energies.[a]

	Neutral with anion geom./hartree	Stable neutral/hartree	Rel. energy/kJ mol^{-1}
H_2CCCCO			
Singlet	−228.15919	−228.17062	30
Triplet	−228.10275	−228.10876	12
HCCCCHO			
Triplet	−228.08296	−228.09244	25
Singlet	−228.07366	−228.07971	16
CC(CH)CHO			
Singlet	−228.08936	−228.09567	17
Triplet	−228.05190	−228.05337	4

[a] Energies at the CCSD(T)aug-cc-pvdz//B3YP/6-31G(d) level of theory, and are unscaled.

Table 6 $^-CR^+$ and $^-NR^+$ spectra of $[CC(CD)CHO]^{-\bullet}$ [*m*/*z* (relative abundance, %)]

$^-CR^+$:	67(13), 66(42), 65(4), 54(7), 53(4), 52(4), 51(6), 50(34), 49(28), 48(12), 43(4), 42(7), 41(5), 39(78), 38(100), 37(53), 36(30), 29(34), 27(1), 26(1), 25(2), 24(4), 15(2), 14(1), 12(1).
$^-NR^+$:	Weak spectrum – smaller peaks (<5% relative abundance) are lost in baseline noise. 67(16), 66(44), 50(15), 49(15), 39(100), 38(73), 37(53), 36(24), 29(18).

The available data show that singlet HCCCCHO only needs 4 kJ mol^{-1} of excess energy to cause rearrangement to HCC(CH)CO. This species is formed with 254 kJ mol^{-1} of excess energy, and may decompose to HCCCH and CO. Alternatively, if HCCCCHO has ≥43 kcal mol^{-1} of excess energy, it may rearrange through HCC(CH)CO to energised H_2CCCCO, which in turn may decompose to H_2CCC and CO (see Fig. 5 and Table 2).

2 The formation and possible rearrangements of CC(CH)CHO and CC(CD)CHO

We have shown that when there are hydrogen substituents at the 1 and 4 positions in a cumulene oxide (as in HCCCCHO) the hydrogen at position 1 can move along the chain in several steps to attach to the end of the chain (for example to form H_2CCCCO). What will happen if neither of the two Hs is attached initially to the terminal C? Will they both move to the terminal carbon, and, if so, in what order? This is a more complex situation than that considered above, and we have chosen to investigate neutral CC(CH)CHO and the deuterium analogue CC(CD)CHO in this regard. The two precursor anions $[CC(CH)CHO]^{-\bullet}$ and $[CC(CD)CHO]^{-\bullet}$ were made by the unequivocal syntheses described in the Experimental section. The data contained in Table 1 show the anions to be stable species. The $^-CR^+$ and $^-NR^+$ spectra of the labelled anion radical are listed in Table 6, while those of the unlabelled derivative are shown in Fig. 6.

The $^-CR^+$ spectra shown in Table 6 and Fig. 6 indicate that the backbone skeletons of the cations are mainly intact. In particular, losses of C_2 (*m*/*z* 42), $CHO^\bullet$ (*m*/*z* 37), together with formation of *m*/*z* 29 (CHO^+) and *m*/*z* 24 ($C_2^{+\bullet}$) are consistent with an unrearranged cation structure $[CC(CH)CHO]^{+\bullet}$. In contrast, losses of $CH^\bullet$ (*m*/*z* 53), CH_2 (*m*/*z* 52) and CO (*m*/*z* 38) are indicative of complex rearrangement. For example, losses of $CH^\bullet$ and CH_2 are characteristic of compounds containing CH and CH_2 at the terminal position. The $^-CR^+$ spectrum of the labelled species is consistent with these observations. The $^-NR^+$ spectra, although weak, are similar to the $^-CR^+$ spectra with the exception that the peaks due to loss of CO are of larger abundance, and those due to CHO^+ (*m*/*z* 29) are smaller in the $^-NR^+$ spectra.

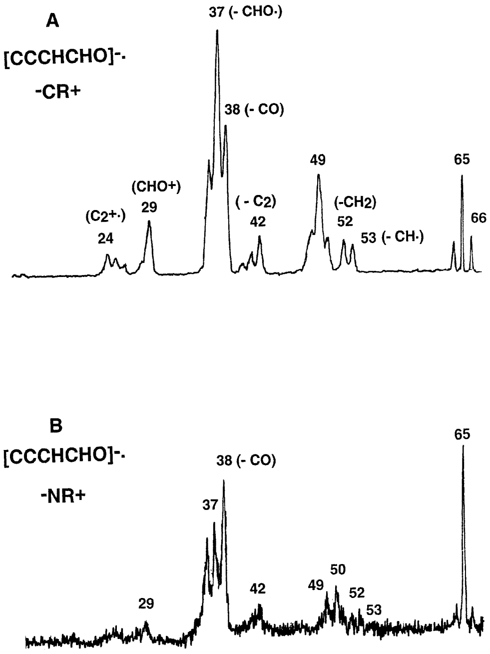
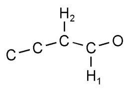
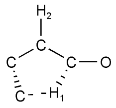


Fig. 6 (**A**) Charge reversal ($^-CR^+$) mass spectrum, and (**B**) neutralisation–reionisation ($^-NR^+$) mass spectrum of $[CCCHCHO]^{-\bullet}$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental section.

There are singlet and triplet forms of CC(CH)CHO. The singlet is the ground state by 107 kJ mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. The singlet is best represented as the valence bond structure : C=C=CH–CH=O, with the CCO bond angle being 123°. The dipole moment of the singlet is 1.44 D, and the adiabatic electron affinity is 2.69 eV. We have undertaken an extensive theoretical survey of possible rearrangement reactions of singlet and triplet CC(CH)CHO. Most of these have barriers in excess of 210 kJ mol^{-1}, and are not considered further here. However one process is worthy of mention. Singlet CC(CH)CHO can rearrange through HCC(CH)CO to H_2CCCCO [see Fig. 7 (*cf.* also Tables 4 and 7)]. The first, and key step involves 1,4-H transfer (barrier 151 kJ mol^{-1}) which occurs in this system (but not for those described earlier) because the C chain is significantly bent in this system. This excess energy is greater than the 17 kJ mol^{-1} (Table 2) provided to the neutral as a consequence of the

Table 7 Data for additional singlet species in Fig. 7[a]

		
State	1A′	
Symmetry	*Cs*	*C*1
Energy/Hartrees	−228.05473	−227.99692
Relative energy/kJ mol $^{-1}$	196	347
Dipole/debye	1.44	
Adiabatic electron affinity/eV	2.69	
Bond length/Å or angle/°		
C1C2[b]	1.496	1.502
C2C3	1.332	1.383
C3C4	1.294	1.329
C1O	1.213	1.150
C1H1	1.106	1.457
C4H1		1.335
C2H2	1.092	1.093
C1C2C3	121.8	110.9
C2C3C4	177.1	98.4
OC1C2	121.6	138.8
H1C1C2	115.4	90.4
H2C2C3	122.7	127.3
C1C2C3C4	0.0	−43.9
OC1C2C3	180.0	−125.8
H1C1C2C3	0.0	33.0
H2C2C3C4	180.0	120.6

[a] Geometries B3LYP/6-31G(d); energies CCSD(T)/aug-cc-pvdz//B3LYP/6-31G(d) including zero point energy correction, scaled by 0.9804.[38] [b] Carbons are numbered 1 to 4; C1 is adjacent to O.

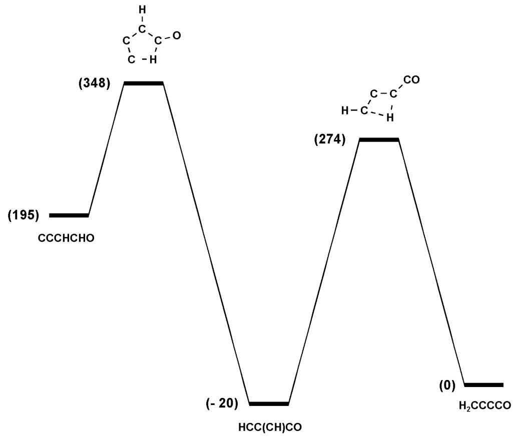


Fig. 7 Reaction coordinates of the lowest energy rearrangement pathways of singlet CCCHCHO to singlet H_2CCCCO. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6- 31G(d) level of theory. Relative energies in kJ mol^{-1}. The structures in this figure show bond connectivities only. For full details of geometries and energies of all species see Tables 4 and 7.

vertical one-electron oxidation. It is however comparable to the excess energies of similar species which are known to undergo rearrangement during neutralisation.[39] The energy may be provided by collisions of the neutral with the collision gas subsequent to the oxidation process.[26] The intermediate HCC(CH)CO formed in this process has up to 366 kJ mol^{-1} of excess energy, which is sufficient for it either to decompose [to HCCCH and CO (a process endothermic by 245 kJ mol^{-1}, see Table 5)], or rearrange to a decomposing H_2CCCCO species.

We have also considered the possible rearrangements involving oxygen transfer: these are high energy processes. For example, the 1,4-oxygen transfer of CC(CH)(CHO) to give 2,3-dehydrofuran has a barrier of 167 kJ mol^{-1} and is endothermic by 106 kJ mol^{-1} at the level of theory used in this study. Cleavage of the HC–O bond in 2,3-dehydrofuran requires the precursor CC(CH)CHO to have an excess energy of ≥214 kJ mol^{-1}. This process is energetically unfavourable compared with that shown in Fig. 7.

Conclusions

1 Vertical one-electron oxidation of $[H_2CCCCO]^{-\bullet}$ yields H_2CCCCO. The majority of these neutrals are stable for the microsecond duration of the $^{-}NR^{+}$ experiment, but some are sufficiently excited to effect loss of CO.

2 Vertical one-electron oxidation of $[HCCCCDO]^{-\bullet}$ yields HCCCCDO neutrals. Some of these are stable for the duration of the $^{-}NR^{+}$ experiment, whereas others undergo facile rearrangement to energised isomers HCC(CD)CO and HDCCCCO, which may decompose by loss of CO.

3 Vertical one electron oxidation of $[CC(CH)CHO]^{-\bullet}$ yields some stable neutrals CC(CH)CHO, together with others which are energised and undergo H rearrangement to yield neutrals HCC(CH)CO and H_2CCCCO. Some of the rearranged products have sufficient excess energy to cause decomposition by loss of CO.

Experimental

A Mass spectrometric methods

For a detailed description of the instrument used, see ref. 27. 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 anions $[CH_2CCCO]^{-\bullet}$ and $[CHCCCDO]^{-\bullet}$ were formed in the chemical ionisation source by the reactions between $O^{-\bullet}$ (formed from N_2O in the ion source[37]) and MeO–CH_2–C≡C–CDO as follows:

$$O^{-\bullet} + MeO–CH_2–C{\equiv}C–CDO \longrightarrow [H_2CCCCO]^{-\bullet} + DO^{\bullet} + MeO^{\bullet}$$

$$O^{-\bullet} + MeO–CH_2–C{\equiv}C–CDO \longrightarrow [HCCCCDO]^{-\bullet} + HO^{\bullet} + MeO^{\bullet}$$

The anions $[CCCHCHO]^{-\bullet}$ and $[CCCDCHO]^{-\bullet}$ were formed in the ion source of the mass spectrometer by the DePuy gas-phase $S_N2(Si)$ processes[40] shown below, using F^- (from SF_6) as the nucleophile.

$$F^{-} + trans\text{-}Me_3SiC{\equiv}C–CH{=}CHOMe \longrightarrow [CC(CH)CHO]^{-\bullet} + Me_3SiF + Me^{\bullet}$$

$$F^{-} + trans\text{-}Me_3SiC{\equiv}C–CD{=}CHOMe \longrightarrow [CC(CD)CHO]^{-\bullet} + Me_3SiF + Me^{\bullet}$$

Typical source conditions were as follows: source temperature 200 °C, repeller voltage −0.5 V, ion extraction voltage 7 kV, mass resolution $m/\Delta m$ ε 1500. The neutral precursor was inserted into the ion source through the septum inlet, which was heated to 120 °C to give a measured pressure of *ca.* 10^{-6} Torr inside the source housing. The reagent gas [N_2O (for $O^{-\bullet}$)] 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 was 10^{-1} Torr. Collisional induced (CID) spectra were determined using B to select the parent anion in each case, 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.[41] Product anion peaks resulting from CID processes were recorded by scanning E.

Neutralisation–reionisation ($^{-}NR^{+}$)[42–44] experiments were performed for mass-selected anions utilising the dual collision cells located between the magnetic and electric sectors. Neutralisation of anions was effected by collisional electron detachment using O_2 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 O_2, (80% transmittance) in the second collision cell. In order to detect a reionisation signal due to the parent neutral, the neutral species must be stable for the one microsecond timeframe of this experiment. Charge reversal ($^-$CR$^+$) spectra[45,46] were recorded using single collision conditions in collision cell 1 (O_2, 80% transmission of main beam).

B The neutral precursors

The neutral MeO–CH_2–C≡C–CDO was available from a previous study.[26] Me_3SiC≡C–CH=CHOMe and Me_3SiC≡C–CD=CHOMe were made by a known method.[47]

C Theoretical methods

Geometry optimisations were carried out with the Becke B3LYP method[48,49] using the 6-31G(d) basis set within the GAUSSIAN 98 suite of programs.[50] Stationary points were characterised as either minima (no imaginary frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were used as a zero-point correction for the electronic energies.[38] We have previously reported the success of the B3LYP method in predicting geometries of unsaturated chain structures; 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 method, CCSD(T) method[52] incorporating the Dunning aug-cc-pVDZ basis set.[53] All calculations were carried out on the Alpha Server at the Australian Partnership for Advanced Computing (APAC) National Facility (Canberra).

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