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# Generation of neutrals from anionic precursors in the gas phase The anionic, neutral and cationic rearrangements of CCCCHO and CCCHCO to HCCCCO

Mark Fitzgerald, Suresh Dua, John H. Bowie*, Andrew M. McAnoy

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

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Dedicated to Helmut Schwarz on the occasion of his 60th birthday and also to celebrate his outstanding contributions to science.

**Abstract**

The anions, neutrals and cations of the isomers HCCCCO, CCCHCO and CCCCHO have been studied by experiment and by theory at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Anions have been synthesised from precursor neutrals in the source of a mass spectrometer. The anion $[HCCCCO]^-$ and (a major proportion of) $[CCCHCO]^-$ retain their bond connectivity when energised, but theoretical calculations predict that singlet $[CCCCHO]^-$ rearranges to singlet $[CCCHCO]^-$ over a barrier of only 28 kJ mol$^{-1}$. However, triplet $[CCCCHO]^-$ is stable under these conditions. Neutralisation/reionisation of $[HCCCCO]^-$ results in the sequential two-electron vertical oxidation $[HCCCCO]^- \rightarrow HCCCCO \rightarrow [HCCCCO]^+$, with the doublet neutral being stable for the microsecond duration of the NR experiment. In contrast, neutralisation of $[CCCHCO]^-$ and $[CCCCHO]^-$ yield HCCCCO in rearrangements which occur during or subsequent to neutralisation of the anions. Two-electron oxidation (charge reversal, $^-CR^+$) of $[CCCHCO]^-$ and $[CCCCHO]^-$ both produce the rearranged cation $[HCCCCO]^+$ in exothermic reactions.
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*Keywords:* Anionic precursors; Gas phase; Neutrals

## 1. 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], while preliminary measurements suggest that $C_5O$ may also be present, but this has yet to be confirmed [9]. Linear $C_5O$ 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 $C_2O$ and $C_3O$ have also been determined [16]. The rotational spectra of $C_nO$ ($n = 2$–9) have been detected in pyrolytic de-

* Corresponding author. Tel.: +61-8-8303-5767; fax: +61-8-8303-4358.
*E-mail address:* john.bowie@adelaide.edu.au (J.H. Bowie).

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composition and pulsed discharge nozzle experiments [17–19].

It has been suggested that the mechanism of formation of the circumstellar molecules $C_3O$ and propynal may be linked via ion molecule chemistry [20] or by photolysis of the cluster $C_3{\cdot}H_2O$ [21–23], and that the reaction $C_3O^{\bullet+} + H_2 \rightarrow C_3HO^+ + H^\bullet$ may provide a stellar pathway for the consumption of $C_3O$ [24]. We have (i) prepared the stable neutrals $C_3O$ [25], HCCCO [26] and CCCHO [26] in the gas phase from charged precursors, (ii) shown that energised CCCHO may rearrange to HCCCO, which has sufficient excess energy of formation to effect dissociation to CO and $C_2H$ [26], and (iii) suggested that HCCCO and CCCHO may co-occur with $C_3O$ and HC≡C–CHO in dark molecular clouds [26].

In contrast to $C_3$ systems, 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 [27], 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 [16,28–31] and HCCCCO [32,33] have been reported. The only $C_4$ cumulene so far be detected in the stellar environment is HCCCC [5,34].

This study is an extension of our previous work on $HC_3O$ isomers. The aims of the present investigation are: (i) to make the neutrals HCCCCO, CCCHCO and CCCCHO from charged precursors in the gas phase, and (ii) investigate the structure and stability of these species by experiment and by molecular modelling, in particular, to ascertain whether energised CCCCHO and CCCHCO rearrange to HCCCCO.

## 2. Experimental

### 2.1. Mass spectrometric methods

For a detailed description of the instrument used, see [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 anions $[HCCCCO]^-$, $[CCCHCO]^-$ and $[CCCCHO]^-$ were formed in the chemical ionisation source by the synthetic procedures shown in Eq. (1) and Eqs. (6) and (8) (Scheme 2). Precursor anions were formed as follows: (i) $[HCCCCO]^-$ from the reaction between $O^{\bullet-}$ (formed from $N_2O$ in the ion source [35]) and $CH_3$–C≡C–$CO_2C_2H_5$, (ii) $[CCCHCO]^-$ from the $S_N2$(Si) reaction [36] between $F^-$ (from $SF_6$ [27]) and $(CH_3)_3$Si–C≡C–CH=$CHOCH_3$, and (iii) $[CCCCHO]^-$ from the reaction between $F^-$ and $(CH_3)_3$SiC≡C–$CH(OCH_3)$(CHO). Full details are shown in Eq. (1) and Scheme 2.

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 120 °C to give a measured pressure of ca. $10^{-6}$ Torr inside the source housing. The reagent gas [either $N_2O$ (for $O^{\bullet-}$) or $SF_6$ (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. 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 [37]. Product anion peaks resulting from CID processes were recorded by scanning E.

Neutralisation–reionisation ($^-NR^+$) [38–40] 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 [41,42] were recorded using single collision conditions in collision cell 1 ($O_2$, 80% transmission of main beam).

### 2.2. Synthetic procedures

$CH_3$–C≡C–$CO_2CH_2CH_3$ is a commercial sample. $CH_3OCH_2$–C≡C–CHO (or CDO) [43] and $(CH_3)_3$Si–C≡C–CH (or CD)=CH–$OCH_3$ [44] were made by reported procedures.

#### 2.2.1. *$(CH_3)_3$Si–C≡C–CH($OCH_3$)–CH($OCH_3$)$_2$ [precursor of unstable $(CH_3)_3$Si–C≡C–CH($OCH_3$)–CHO]*

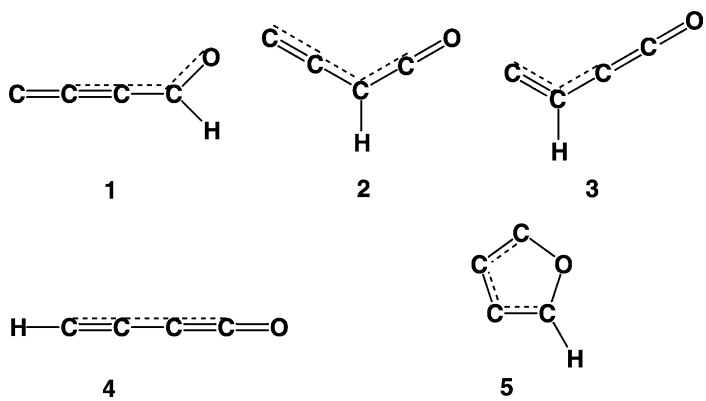
To trimethylsilylacetylene (0.62 g) in anhydrous tetrahydrofuran (25 $cm^3$) at 0 °C under nitrogen was added ethylmagnesium bromide [from bromoethane (0.90 g) and magnesium (0.7 g) in anhydrous diethyl ether (30 $cm^3$)]. This mixture was allowed to stir at 0 °C for 20 min, and then added to 1,2-dichloro-1,2-dimethoxyethane (1.0 g) [45] over a period of 15 min. The mixture was allowed to stir at 0 °C for 30 min, then at 20 °C for 2 h, water (1 $cm^3$) and aqueous hydrogen chloride (10%, 20 $cm^3$) were added at 0 °C, the mixture stirred at 0 °C for 1 h, the organic layer separated, dried ($MgSO_4$) and the solvent removed in vacuo. The residue was distilled at 118–120 °C/40 mmHg giving the product as a colourless oil (0.91 g, 51% yield). Mass spectrum: $M^{\bullet+}$ [216, not present] [$(M^{\bullet+} - CH_3O^{\bullet})^+$ (24%)] {*m/z* 75 [$(CH_3O)_2$–$CH^+$] 100%}. Mass measurement on the $(M^{\bullet+} - CH_3O^{\bullet})^+$ ion, found 185.0102; $C_9H_{17}O_2Si$ requires 185.0098. $^1$H NMR (200 MHz, $CDCl_3$, $\delta$): 0.18 [9H, s, Si($CH_3$)$_3$], 3.44 (3H, s, $OCH_3$), 3.45 (3H, s, $OCH_3$), 3.49 (3H, s, $OCH_3$), 4.01 [1H, d ($J$ = 6.1 Hz), HC], 4.35 [1H, d ($J$ = 6.1 Hz), H–C($OCH_3$)$_2$]. $^{13}$C NMR (200 MHz, $CDCl_3$, $\delta$): 0.00, 54.47, 55.57, 56.47, 72.47, 92.11, 100.48.

### 2.3. Theoretical methods

Geometry optimisations were carried out with the Becke 3LYP method [46,47] using the 6-31G(d) basis set within the GAUSSIAN 98 suite of programs [48]. 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. 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 [49]. More accurate energies for the B3LYP geometries were determined using the couple cluster method, CCSD(T) method [50] using the Dunning aug-cc-pVDZ basis set [51]. All calculations were carried out on the Alpha Server at the Australian Partnership for Advanced Computing (APAC) National Facility (Canberra).

## 3. Results and discussion

The aims of this project are to form, from anionic precursors, the neutral radicals HCCCCO, CCCHCO and CCCCHO, and to study the possible interconversion of these molecules. We first need to determine whether these three structures, together with any other isomers containing CCCCO bond connectivity (which might be implicated in the possible rearrangement of CCCCHO or CCCHCO to HCCCCO) are stable species. Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory indicate that there are five such structures. The global minimum on the neutral potential surface corresponds to linear HCCCCO represented by the valence structure **4** shown in Scheme 1: this is the only isomer to have been reported previously [32]. The other structures **1**–**3** and **5**, lie 193, 91, 325 and 379 kJ $mol^{-1}$, respectively, above **4** at the level of theory used for this study. Full details of the




Scheme 1.

structures and energies of these species are recorded in Table 1.

The next task is to determine whether there are stable anions from which the neutral species shown in Scheme 1 can be formed, and if so, which of these can be synthesised unambiguously from accessible neutral molecules of defined bond connectivity. There are many other anion isomers $C_4HO$, including the cyclic species formed by loss of $MeO^{\bullet}$ from the 3-carbomethoxycyclopropen-3-yl anion [52]. These are not related to the systems under study, and have not been considered further. There are minima on the anion potential surfaces for the singlet and triplet states of all of the anions corresponding to neutrals **1**, **2**, **4** and **5**. Anion **3** has only a stable triplet state; the singlet is unstable, undergoing rearrangement to singlet $\mathbf{4}^-$. Full details of the geometries and energies of all nine of these stable anions are recorded in Table 2. The triplet states are the ground states of $[CCCCHO]^-$ (**1**) and $[CCHCCO]^-$ (**3**). The singlet states are the ground states of **2**, **4** and **5**, with that of $[HCCCCO]^-$ ($^1\mathbf{4}^-$) being the global minimum of both anion potential energy surfaces. Since the geometries of each neutral/anion pair are quite similar, each of the neutrals **1**–**5** should be accessible by Franck–Condon vertical one-electron oxidation of the appropriate anion. A particular example of this is the one-electron vertical oxidation of singlet $[HCCCCO]^-$ to doublet HCCCCO. In this case, the excess Franck–Condon energy of the neutral as a consequence of the vertical process is only $5\,kJ\,mol^{-1}$ (the difference in energy between stable doublet HCCCCO and of HCCCCO with the singlet anion geometry on the neutral reaction coordinate).

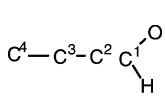
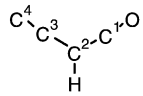
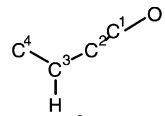
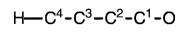
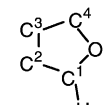
### 3.1. The syntheses of $[CCCCHO]^-$ ($\mathbf{1}^-$), $[CCCHCO]^-$ ($\mathbf{2}^-$) and $[HCCCCO]^-$ ($\mathbf{4}^-$)

To design unequivocal syntheses of all of the anions $\mathbf{1}^-$ to $\mathbf{5}^-$ is a difficult undertaking. We have been unable to devise viable routes to $\mathbf{3}^-$ or $\mathbf{5}^-$. However, the synthesis of $[HCCCCO]^-$ ($\mathbf{4}^-$) is straightforward and may be effected by the standard $O^{\bullet -}$ reaction [35] shown in Eq. (1).

$$\begin{aligned} &CH_3\text{–}C{\equiv}C\text{–}CO\text{–}OEt + O^{\bullet -} \rightarrow \\ &[HC\text{–}C{\equiv}C\text{–}CO\text{–}OEt]^{\bullet -} + H_2O \rightarrow [HCCCCO]^- \\ &\qquad + EtO^{\bullet} + H_2O \end{aligned} \tag{1}$$

The preparation of $[CCCCHO]^-$ ($\mathbf{1}^-$) is challenging and in making it, we also, serendipitiously, effected the synthesis of the third isomer $[CCCHCO]^-$ ($\mathbf{2}^-$). We first attempted to prepare $[CCCCHO]^-$ by 1,1-elimination of methanol from the precursor anion (formed by deprotonation of $CH_3OCH_2C{\equiv}CCHO$) shown in Eq. (2) (Scheme 2). The expected process did not occur; instead, loss of the elements of methanol gave $[HCCCCO]^-$ (Eq. (3)), a process confirmed by the deuterium labelling experiment summarised in Eq. (4). We next attempted the reaction shown in

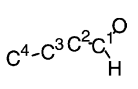
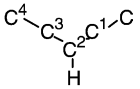
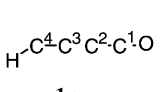
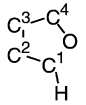
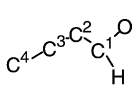
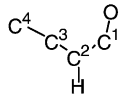
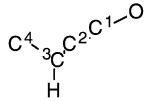
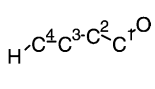
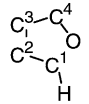
Table 1
Energies and geometries of neutrals **1**–**5**

| Neutral |  **2$_1$** |  **2$_2$** |  **2$_3$** |  **2$_4$** |  **2$_5$** |
|---|---|---|---|---|---|
| State | $^2A''$ | $^2A''$ | $^2A''$ | | $^2A'$ |
| Symmetry | Cs | Cs | Cs | C*V | Cs |
| Energy (Hartrees)[a] | −227.41608 | −227.45506 | −227.36593 | −227.48953 | −227.34524 |
| Dipole moment (Debye)[b] | 2.21 | 4.85 | 1.53 | 2.62 | 1.47 |
| Adiabatic electron affinity (eV) | 2.61 | 2.62 | 2.49 | 2.68 | 2.59 |
| Bond length (Å)[b] or angle (°)[b] | | | | | |
| $C^1C^2$ | 1.415 | 1.356 | 1.266 | 1.272 | 1.361 |
| $C^2C^3$ | 1.263 | 1.382 | 1.390 | 1.324 | 1.332 |
| $C^3C^4$ | 1.322 | 1.286 | 1.321 | 1.233 | 1.362 |
| $C^1O$ | 1.229 | 1.156 | 1.191 | 1.185 | 1.380 |
| $C^4O$ | | | | | 1.369 |
| $C^1H$ | 1.106 | | | | 1.076 |
| $C^2H$ | | 1.090 | | | |
| $C^3H$ | | | 1.113 | | |
| $C^4H$ | | | | 1.066 | |
| $C^1C^2C^3$ | 178.7 | 116.0 | 179.9 | 180.0 | 116.5 |
| $C^2C^3C^4$ | 179.1 | 178.8 | 142.3 | 180.0 | 99.5 |
| $OC^1C^2$ | 121.6 | 177.8 | 179.8 | 180.0 | 104.6 |
| $HC^1C^2$ | 115.3 | | | | 136.9 |
| $HC^2C^3$ | | 125.8 | | | |
| $HC^3C^4$ | | | 98.7 | | |
| $HC^4C^3$ | | | | 180.0 | |
| $C^1C^2C^3C^4$ | 180.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $OC^1C^2C^3$ | 0.0 | 0.0 | 180.0 | 0.0 | 0.0 |
| $HC^1C^2C^3$ | 180.0 | | | | 180.0 |
| $HC^2C^3C^4$ | | 180.0 | | | |
| $HC^3C^2C^1$ | | | 180.0 | | |
| $HC^4C^3C^2$ | | | | 0.0 | |

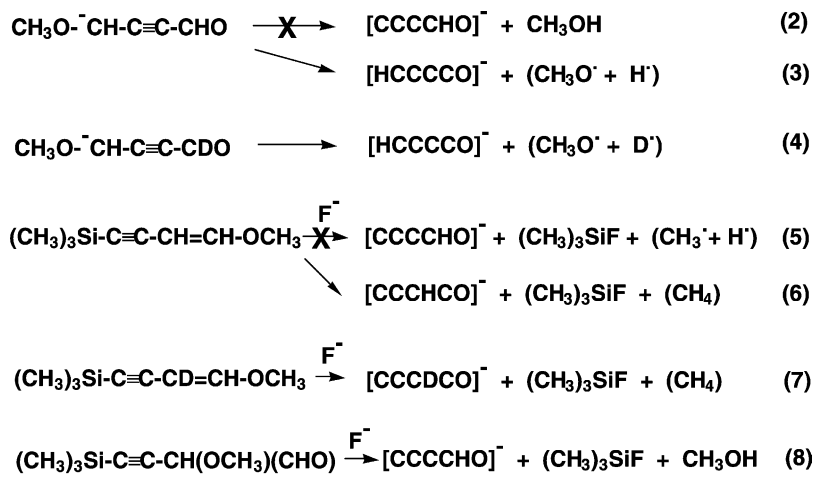
[a] CCSD(T)/aug-cc-pVDZ level of theory including zero-point energy (B3LYP/6-31G(d), scaled by 0.9804).
[b] B3LYP/6-31G(d) level of theory.

Eq. (5). Here, the $S_N2$(Si) [36] reaction of $(CH_3)_3SiC{\equiv}C{-}CH{=}CH{-}OCH_3$ with $F^-$ yields $^-C \equiv C{-}CH{=}CH{-}OCH_3$ which was then expected to produce $[CCC{-}CHO]^-$ by 1,3-elimination of $CH_3^\bullet$ and $H^\bullet$ (Eq. (5)). This reaction did not occur, instead, 1,1-elimination of the elements of methane effected the formation of $[CCCHCO]^-$ as shown in Eq. (6), a process substantiated by the deuterium labelling experiment shown in Eq. (7). Finally, the synthesis of $[CCCCHO]^-$ was achieved by the following procedure. Introduction of $(CH_3)_3Si{-}C{\equiv}C{-}CH(OCH_3){-}CH(OCH_3)_2$ into the mass spectrometer via the septum inlet (heated to 100 °C) causes conversion of the acetal to produce the unstable aldehyde $(CH_3)_3Si{-}C{\equiv}C{-}CH(OCH_3)(CHO)$ which undergoes the $S_N2$(Si) process with $F^-$ in the ion source to furnish $^-C \equiv C{-}CH(OCH_3)(CHO)$. This anion undergoes the expected 1,1-elimination of the elements of methanol to form $[CCCCHO]^-$ (Eq. (8)). We were not able to synthesise a deuterium labelled precursor in order to substantiate the formation of this product anion using labelling studies, but the CID spectrum of this anion shows it to be $[CCCCHO]^-$ rather than $[CCCHCO]^-$ (see Scheme 2).

Table 2
Energies and geometries of anions

| Anion |  $^1$1 |  $^1$2 |  $^1$4 |  $^1$5 |  $^3$1 |  $^3$2 |  $^3$3 |  $^3$4 |  $^3$5 |
|---|---|---|---|---|---|---|---|---|---|
| State | $^1$A′ | $^1$A′ | $^1$A′ | $^1$A′ | $^3$A″ | $^3$A″ | $^3$A″ | $^3$A″ | $^3$A′ |
| Symmetry | Cs | Cs | Cs | Cs | Cs | Cs | Cs | Cs | Cs |
| Energy (Hartrees)[a] | −227.50902 | −227.55146 | −227.58785 | −277.44029 | −227.51184 | −227.51553 | −227.45740 | −227.50174 | −227.41706 |
| Dipole moment (Debye)[b] | 2.76 | 7.71 | 1.27 | 4.27 | 3.85 | 4.49 | 3.56 | 1.64 | 2.61 |
| Bond length (Å)[b] or angle (°)[b] | | | | | | | | | |
| $C^1C^2$ | 1.363 | 1.325 | 1.251 | 1.365 | 1.409 | 1.440 | 1.261 | 1.388 | 1.367 |
| $C^2C^3$ | 1.303 | 1.433 | 1.35 | 1.381 | 1.310 | 1.380 | 1.393 | 1.295 | 1.404 |
| $C^3C^4$ | 1.293 | 1.254 | 1.234 | 1.444 | 1.303 | 1.276 | 1.404 | 1.321 | 1.336 |
| $C^1O$ | 1.261 | 1.191 | 1.222 | 1.355 | 1.248 | 1.219 | 1.219 | 1.228 | 1.399 |
| $C^4O$ | | | | 1.500 | | | | | 1.402 |
| $C^1H$ | 1.130 | | | 1.083 | 1.122 | | | | 1.087 |
| $C^2H$ | | 1.098 | | | | 1.094 | | | |
| $C^3H$ | | | | | | | 1.114 | | |
| $C^4H$ | | | 1.065 | | | | | 1.102 | |
| $C^1C^2C^3$ | 175.2 | 122.3 | 177.1 | 131.2 | 145.4 | 126.2 | 172.4 | 146.9 | 108.3 |
| $C^2C^3C^4$ | 179.7 | 179.4 | 177.2 | 83.8 | 175.1 | 178.8 | 126.2 | 165.5 | 105.0 |
| $OC^1C^2$ | 132.3 | 178.8 | 179.4 | 102.9 | 127.8 | 132.2 | 177.2 | 136.3 | 110.5 |
| $HC^1C^2$ | 197.9 | | | 135.2 | 114.2 | | | | 134.7 |
| $HC^2C^3$ | | 122.8 | | | | 119.4 | | | |
| $HC^3C^4$ | | | | | | | 119.0 | | |
| $HC^4C^3$ | | | 164.2 | | | | | 119.3 | |
| $C^1C^2C^3C^4$ | 0.0 | 180.0 | 180.0 | 0.0 | 180.0 | 180.0 | 0.0 | 180.0 | 0.0 |
| $OC^1C^2C^3$ | 180.0 | 0.0 | 180.0 | 0.0 | 180.0 | 0.0 | 180.0 | 180.0 | 0.0 |
| $HC^1C^2C^3$ | 0.0 | | | 180.0 | 0.0 | | | | 180.0 |
| $HC^2C^3C^4$ | | 0.0 | | | | 0.0 | | | |
| $HC^3C^2C^1$ | | | | | | | 180.0 | | |
| $HC^4C^3C^2$ | | | 180.0 | | | | | 180.0 | |

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




Scheme 2.

Having synthesised $[CCCCHO]^-$ (**1**$^-$), $[CCCHCO]^-$ (**2**$^-$) and $[HCCCCO]^-$ (**4**$^-$), it is now necessary to determine whether any of these anions rearrange to another isomer under the collision conditions that will be used to convert them into the required neutral. It is unusual for a cumulene or heterocumulene anion to rearrange under collisional conditions: indeed, we have only observed such a scenario once before (for the rearrangement of $[CC(O)(CN)]^-$ to $[NCCCO]^-$ [53]). Normally, a combination of the data obtained from the CID (negative ion) mass spectrum of the anion and its charge reversal [$^-CR^+$, two-electron vertical oxidation of the anion to a (decomposing) cation] provides a useful probe to determine the stability or otherwise of the anion. In this case, the results from the CID spectra of $[CCCHCO]^-$ and $[HCCCCO]^-$ are clear cut, but those from $[CCCCHO]^-$ are equivocal. The CID mass spectra (MS/MS) of all three anions are recorded in Table 3. All show loss of H$^\bullet$, while the spectrum of $[CCCHCO]^-$ also exhibits a significant peak corresponding to the loss of CO. However, for $[CCCCHO]^-$ and $[HCCCCO]^-$, apart from the loss of H$^\bullet$, peaks resulting from other decompositions are either not seen at all, or are so small as to be just visible over background noise. With the mass spectrometer operating at maximum sensitivity, there appear to be three other fragmentations of $[HCCCCO]^-$ just visible on a very noisy background, viz. peaks resulting from the losses of HC$^\bullet$, $HC_2^\bullet$ and CO [54]. These decompositions are in accordance with a structure $[HCCCCO]^-$ for the anion. Under exactly the same conditions, there is arguably a small peak at background noise level in the CID spectrum of $[CCCCHO]^-$ due to loss of CO, but it is not possible to make a definite assignment on this evidence. Apart from $[(M-H)^- - H^\bullet]^-$, there are no other peaks, not even one corresponding to the loss of $^\bullet$CHO expected from $[CCCCHO]^-$. One thing that does follow from these data, is that the product anion of Eq. (8) must be $[CCCCHO]^-$ (the likely product because deprotonation at $C^2$ rather than $C^1$ is favoured by about 120 kJ mol$^{-1}$). In principle, there are two possible anions which might originate from the precursor shown in Eq. (8), namely the required $[CCCCHO]^-$ or the alternative species $[CCCHCO]^-$. The latter anion has been formed by the process shown in Eq. (6), and its CID spectrum shows pronounced loss of CO (see Table 3). The CID

Table 3
Fragment anions in the CID spectra of **1**$^-$, **2**$^-$ and **4**$^-$

| | |
|---|---|
| $[CCCCHO]^-$ | 64(−H$^\bullet$)100, 37(−CO)<0.1 |
| $[CCCHCO]^-$ | 64(−H$^\bullet$)100, 37(−CO)8 |
| $[HCCCCO]^-$ | 64(−H$^\bullet$)100, 53(−HC$^\bullet$)≈0.1, 40(−$HC_2^\bullet$)≈0.1, 37(CO)≈0.1 |

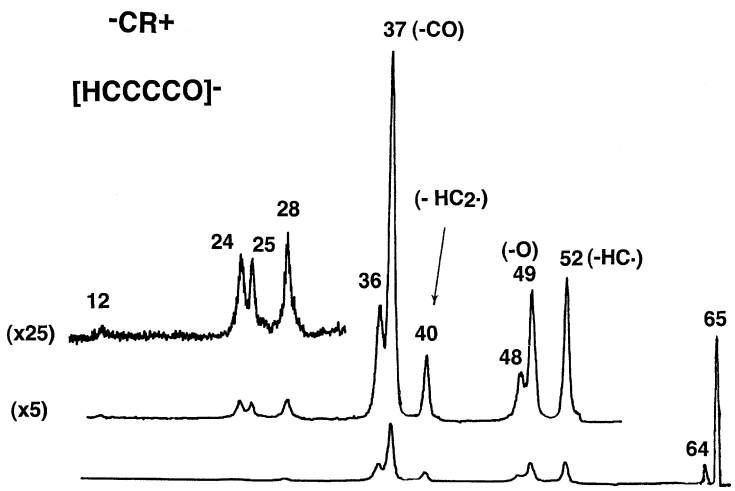



Fig. 1. Charge reversal ($^{-}CR^{+}$) spectrum of $[HCCCCO]^{-}$. VG ZAB 2HF mass spectrometer. For experimental conditions see Section 2.

spectrum of the anionic product of Eq. (8) does not show major loss of CO, thus it cannot correspond to $[CCCHCO]^{-}$.

The $^{-}CR^{+}$ spectra of $[HCCCCO]^{-}$, $[CCCHCO]^{-}$ and $[CCCCHO]^{-}$ are identical. The $^{-}CR^{+}$ spectrum of $[HCCCCO]^{-}$ is shown in Fig. 1. The major peaks in each $^{-}CR^{+}$ spectrum are produced by competitive losses of $H^{\bullet}$, C, O, $HC_2^{\bullet}$, CO, and $HC_4^{\bullet}$. These fragmentations are in accordance with a decomposing cation of connectivity HCCCCO. Other peaks observed in the $^{-}CR^{+}$ spectra are probably formed by consecutive processes, e.g., *m*/*z* 36 $[-(CO + H^{\bullet})]$ and 24 $[-(C_2O + H^{\bullet})]$. The data, to date, clearly indicate that $[HCCCCO]^{-}$ retains its skeletal integrity during both the CID and $^{-}CR^{+}$ processes. In contrast, the CID spectrum of $[CCCCHO]^{-}$ provides no structural data at all, but this spectrum is different from those of $[CCCHCO]^{-}$ and $[HCCCCO]^{-}$. The $^{-}CR^{+}$ spectra of $[CCCCHO]^{-}$ and $[CCCHCO]^{-}$ are the same as that of $[HCCCCO]^{-}$. This observation taken together with data from the CID spectra of the three anions (see above) suggests that major rearrangement occurs at the cation stage, but cannot eliminate the possibility of some rearrangement of precursor anions.

### *3.2. The possible rearrangements of $[CCCCHO]^{-}$ and $[CCCHCO]^{-}$ to $[HCCCCO]^{-}$*

The experiments described above do not indicate whether the anion $[CCCCHO]^{-}$ rearranges to another isomer under the conditions of collisional activation. Thus, we have investigated the anion potential surfaces at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Since there are both singlet and triplet forms of each of $\mathbf{1}^{-}$, $\mathbf{2}^{-}$, $\mathbf{4}^{-}$ and $\mathbf{5}^{-}$ (only the triplet form of $\mathbf{3}^{-}$ is stable) we have considered reaction coordinates on both the singlet and triplet anion potential surfaces. The results of these computations are shown in Figs. 2 and 3. Full details of the structures and energies of anions shown in Figs. 2 and 3 are given in Table 2: similar data for transition states are listed in Table 4.

There are two types of process by which $[CCCCHO]^{-}$ ($\mathbf{1}^{-}$) may rearrange. The first involves H migration along the C chain and is illustrated in Fig. 2, while the second involves cyclisation of O at the terminal C (Fig. 3). In these figures, the energy of either singlet or triplet $[CCCCHO]^{-}$ (as appropriate) has been designated as a nominal 0 kJ mol$^{-1}$. It must

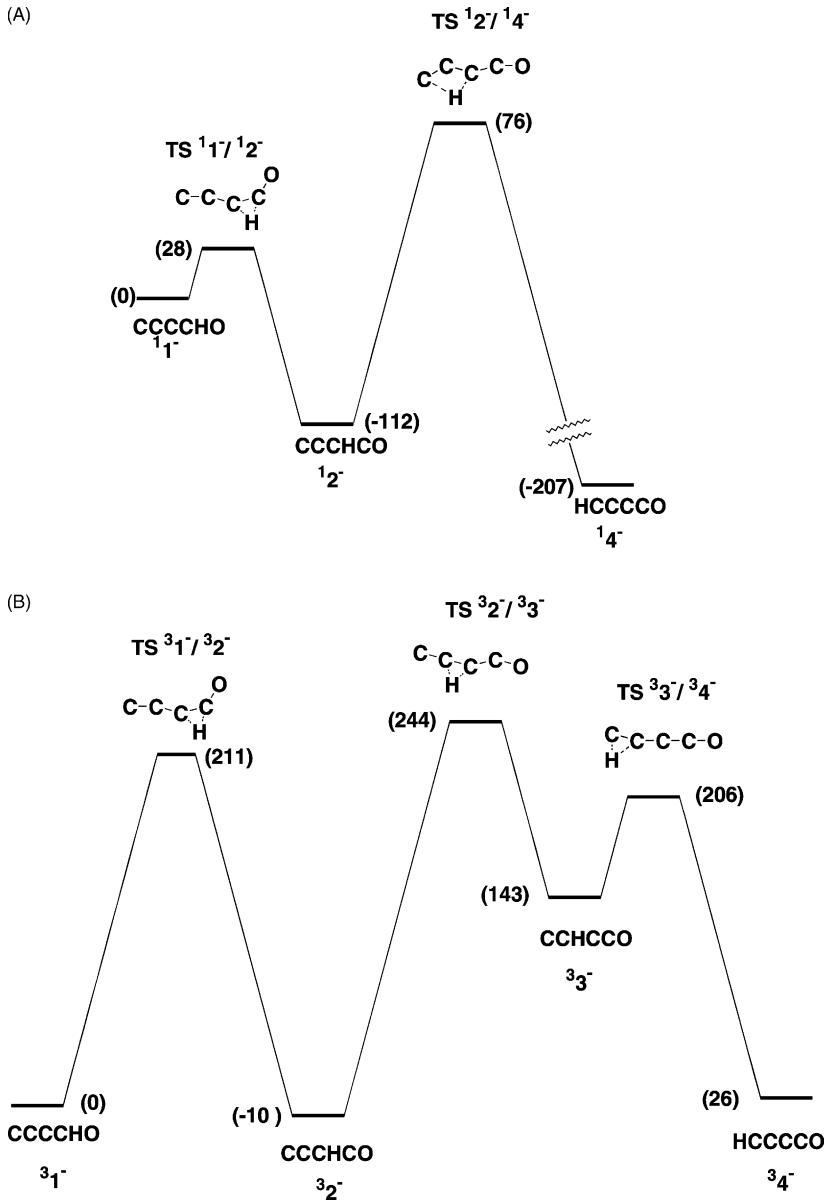



Fig. 2. Possible rearrangement pathways of (A) singlet and (B) triplet $[CCCCHO]^-$ and $[CCCHCO]^-$ to $[HCCCCO]^-$ involving H transfer. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Energies in kJ mol$^{-1}$ with that of $[CCCCHO]^-$ indicated as 0 kJ mol$^{-1}$ in each case. Full details of the geometries and energies of minima on the potential surfaces are recorded in Table 2. Similar details of transition states are listed in Table 4.

also be noted that the triplet state of $[CCCCHO]^-$ is the ground state by only 8 kJ mol$^{-1}$, whereas for $[HCCCCO]^-$, the singlet is the ground state by 226 kJ mol$^{-1}$ (Table 2).

It can be seen in Fig. 2A that $^1$**1**$^-$ needs only 28 kJ mol$^{-1}$ to surmount the barrier to $^1$2$^-$ ($-$112 kJ mol$^{-1}$). Thus, it seems likely that a high proportion of energised singlet species $[CCCCHO]^-$

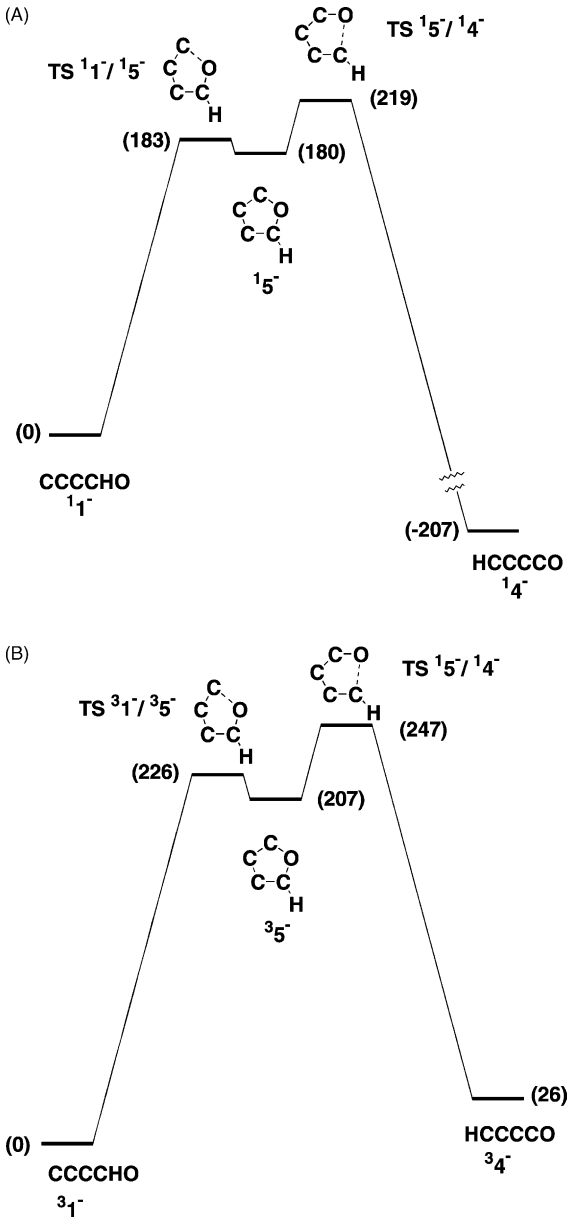



Fig. 3. Rearrangement pathways of (A) singlet and (B) triplet $[CCCCHO]^-$ to $[HCCCCO]^-$ involving O cyclisation to the terminal C. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Energies in kJ mol$^{-1}$ with that of $[CCCCHO]^-$ indicated as 0 kJ mol$^{-1}$ in each case. Full details of the geometries and energies of minima on the potential surfaces are recorded in Table 2. Similar details of transition states are listed in Table 4.

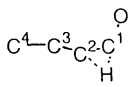
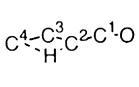
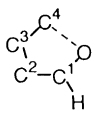
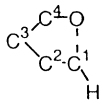
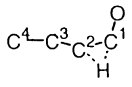
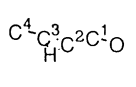
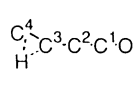
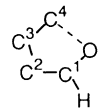
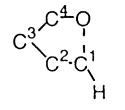
($^1$1$^-$) will convert to singlet $[CCCHCO]^-$ ($^1$2$^-$). Should an equilibrium exist between $^1$1$^-$ and $^1$2$^-$, almost all of the molecules in the equilibrium mixture will correspond to $^1$2$^-$. Some of the species $^1$2$^-$ may have sufficient energy to (i) decompose to $[HCCC]^-$ and CO [this requires 166 kJ mol$^{-1}$ (Table 5)], or (ii) interconvert to $[HCCCCO]^-$ ($^1$4$^-$) [barrier 188 kJ mol$^{-1}$ (Fig. 2A)]. The rearrangement is interesting: here, the H migrates directly from $C^2$ to $C^4$ via a four-centre transition state. If ions $^1$4$^-$ are formed, they may have excess energies of up to 283 kJ mol$^{-1}$ (see Fig. 2A), an energy which is sufficient to cause dissociation to $[HCCC]^-$ and CO (see Table 5).

Since the singlet and triplet states of $[CCCCHO]^-$ have very similar energies, it is also necessary to consider the analogous triplet rearrangement shown in Fig. 2B. In this case, the rearrangement proceeds by three consecutive H migrations. However, this reaction requires triplet $[CCCCHO]^-$ to have an excess energy of at least 244 kJ mol$^{-1}$; this reaction is energetically unfavourable with respect to that of the singlet anion shown in Fig. 2A. Therefore, the triplet state of $[CCCCHO]^-$ is likely to be stable under conditions of collisional activation, unless the triplet undergoes spin crossing to form a rearranging singlet $[CCCCHO]^-$.

Possible conversions of singlet and triplet $[CCCCHO]^-$ (**1**$^-$) through the cyclic intermediates **5**$^-$ to singlet and triplet $[HCCCCO]^-$ (**4**$^-$) are shown in Fig. 3A and B. These processes require 219 and 247 kJ mol$^{-1}$ of excess energy, are energetically unfavourable in comparison to those depicted in Fig. 2, and would seem unlikely mechanistic possibilities.

We conclude that (i) singlet and triplet $[HCCCCO]^-$ (**4**$^-$) are stable under conditions of collisional activation (conditions analogous to those required to effect Franck–Condon vertical oxidation of the anion to the neutral), (ii) some energised singlet species $[CCCHCO]^-$ ($^1$2$^-$) might interconvert to singlet $[HCCCCO]^-$ ($^1$4$^-$), but the corresponding triplet should be stable, and (iii) $[CCCCHO]^-$ ($^1$1$^-$) can convert to singlet $[CCCHCO]^-$ ($^1$2$^-$), but the corresponding triplet should be stable unless spin crossing converts $^3$1$^-$ to $^1$1$^-$.

Table 4
Energies and geometries for transition states shown in Figs. 2 and 3

| Anion |  TS $^{1}1/^{1}2$ |  TS $^{1}2/^{1}4$ |  TS $^{1}1/^{1}5$ |  TS $^{1}5/^{1}4$ |  TS $^{3}1/^{3}2$ |  TS $^{3}2/^{3}3$ |  TS $^{3}3/^{3}4$ |  TS $^{3}1/^{3}5$ |  TS $^{3}5/^{3}4$ |
|---|---|---|---|---|---|---|---|---|---|
| State | $^{1}A'$ | $^{1}A'$ | $^{1}A'$ | | | | | | |
| Symmetry | Cs | Cs | Cs | C1 | C1 | C1 | C1 | C1 | C1 |
| Energy (Hartrees)[a] | −227.49826 | −227.47995 | −227.43917 | −227.42552 | −227.43156 | −227.41910 | −227.43355 | −227.42588 | −227.41706 |
| Bond length (Å)[b] or angle (°)[b] | | | | | | | | | |
| $C^{1}C^{2}$ | 1.289 | 1.260 | 1.358 | 1.375 | 1.404 | 1.363 | 1.268 | 1.397 | 1.338 |
| $C^{2}C^{3}$ | 1.353 | 1.410 | 1.360 | 1.334 | 1.345 | 1.365 | 1.366 | 1.375 | 1.390 |
| $C^{3}C^{4}$ | 1.264 | 1.275 | 1.419 | 1.451 | 1.282 | 1.320 | 1.427 | 1.366 | 1.382 |
| $C^{1}O$ | 1.232 | 1.216 | 1.338 | 1.908 | 1.239 | 1.222 | 1.218 | 1.315 | 1.803 |
| $O^{4}C$ | | | 1.690 | 1.311 | | | | 1.773 | 1.287 |
| $C^{1}H$ | 1.284 | | 1.085 | 1.097 | 1.355 | | | 1.097 | 1.085 |
| $C^{2}H$ | 1.488 | 1.342 | | | 1.436 | 1.411 | | | |
| $C^{3}H$ | | | | | | 1.309 | 1.263 | | |
| $C^{4}H$ | | 2.139 | | | | | 1.377 | | |
| $C^{1}C^{2}C^{3}$ | 177.4 | 172.5 | 133.3 | 96.9 | 146.4 | 144.9 | 169.6 | 107.4 | 110.9 |
| $C^{2}C^{3}C^{4}$ | 179.2 | 176.0 | 88.8 | 132.2 | 173.0 | 171.9 | 132.9 | 113.5 | 108.8 |
| $OC^{1}C^{2}$ | 167.2 | 178.1 | 104.1 | 103.2 | 136.1 | 143.4 | 178.6 | 116.9 | 103.6 |
| $HC^{1}C^{2}$ | 68.5 | | 133.0 | 123.8 | 62.7 | | | 127.0 | 136.9 |
| $HC^{2}C^{3}$ | | 54.0 | | | | 56.2 | | | |
| $HC^{3}C^{4}$ | | | | | | | 61.2 | | |
| $C^{1}C^{2}C^{3}C^{4}$ | 180.0 | 180.0 | 0.0 | 28.3 | −179.7 | 63.8 | 160.4 | 17.0 | −8.9 |
| $OC^{1}C^{2}C^{3}$ | 180.0 | 180.0 | 0.0 | −6.7 | 0.4 | 136.7 | 128.1 | −4.3 | 8.0 |
| $HC^{1}C^{2}C^{3}$ | 0.0 | | 180.0 | 112.3 | −119.8 | | | 178.8 | 136.5 |
| $HC^{2}C^{3}C^{4}$ | | 0.0 | | | | −163.1 | | | |
| $HC^{3}C^{2}C^{1}$ | | | | | | | 77.4 | | |

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

Table 5
Dissociation energies (kJ mol$^{-1}$) for anions, cations and neutrals

| | |
|---|---|
| $^1HCCCCO^- \rightarrow {}^1HCCC^- + CO$ | 261 |
| $^1CCCHCO^- \rightarrow {}^1HCCC^- + CO$ | 166 |
| $HCCCCO \rightarrow CCCCO + H$ | 441 |
| $HCCCCO \rightarrow HCCC + CO$ | 174 |
| $HCCCCO \rightarrow HCCCC + {}^3O$ | 636 |
| $CCCCHO \rightarrow CCCCO + H$ | 249 |
| $CCCCHO \rightarrow CCC + CHO$ | 219 |
| $^1HCCCCO^+ \rightarrow {}^1HCCC^+ + CO$ | 142 |
| $^3HCCCCO^+ \rightarrow {}^3HCCC^+ + CO$ | 369 |

CCSDT/aug-cc-pVDZ//B3LYP-6-31G(d) level of theory. Energy values were determined from the following theoretically calculated values (Hartrees): $HCCC^- = -114.41935$, $CO = -113.06894$, $CCCCO = -226.82180$, $H = -0.49933$, $HCCCC = -152.32176$, $^3O = -74.92565$, $CCC = -113.74598$, $CHO = -113.58699$, $^3HCCC^+ = -113.96123$, $^1HCCC^+ = -114.02679$.

### 3.3. Conversion of anions to neutrals by vertical oxidation

We have shown above that $[HCCCCO]^-$ is stable under the conditions of collisional activation and that the cation $[HCCCCO]^+$ also retains its structural integrity during and following the charge reversal process. However, both $[CCCCHO]^-$ and $[CCCHCO]^-$ may undergo partial rearrangement at the anion stage and both of the analogous cations rearrange to $[HCCCCO]^+$ during or following the two-electron oxidation of the charge reversal process. The $^-NR^+$ spectra of the three anions are the same within experimental error, and, the same as the $^-CR^+$ spectra. The $^-NR^+$ spectrum of $[HCCCCO]^-$ is shown for illustration purposes in Fig. 4: this should be compared with Fig. 1. What is clear, is that neutral HCCCCO is stable for the microsecond duration of the neutralisation reionisation experiment, and there is no significant decomposition pathway of this neutral (see Table 5 for the thermodynamics of some neutral decomposition processes). Unfortunately, the identical NR and CR spectra provide no information concerning the possibility of rearrangements of CCCHCO and CCCCHO, but they do indicate that there is no major decomposition of the neutrals to other neutrals during their microsecond lifetime.

### 3.4. Possible rearrangement of the neutrals CCCCHO and CCCHCO

Since the experimental data do not provide any information concerning possible rearrangements of the neutrals CCCCHO and CCCHCO, we have

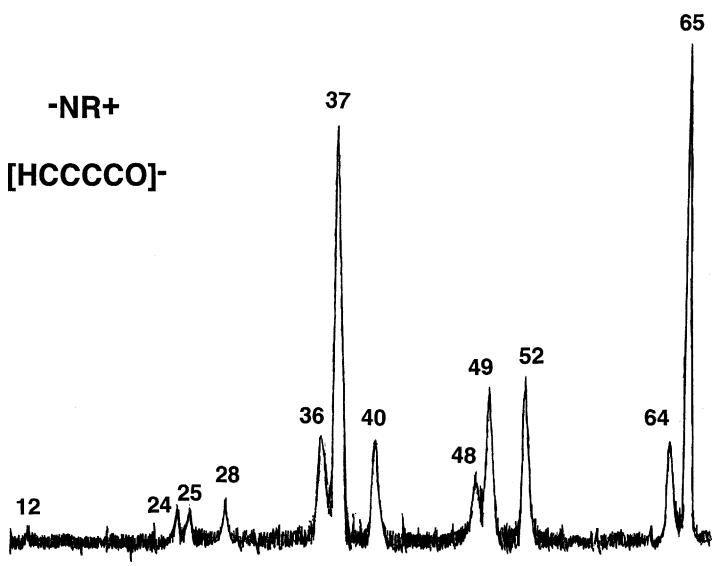



Fig. 4. Neutralisation reionisation ($^-NR^+$) spectrum of $[HCCCCO]^-$. VG ZAB 2HF mass spectrometer. For experimental conditions see Section 2.

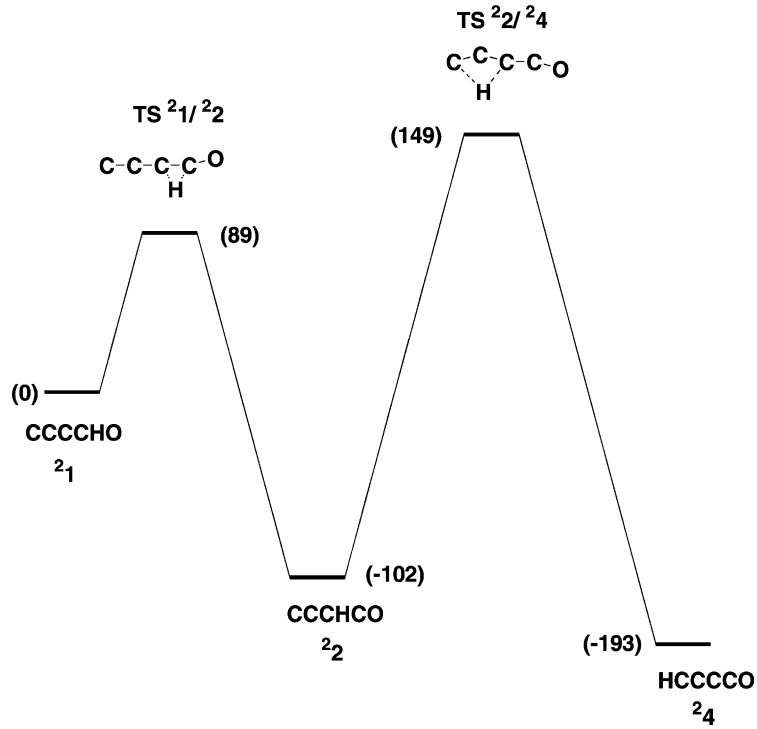



Fig. 5. Rearrangement pathways of doublet CCCCHO and CCCHCO to HCCCCO. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Energies in kJ mol$^{-1}$ with that of CCCCHO indicated a nominal 0 kJ mol$^{-1}$. Full details of the geometries and energies of minima on the potential surfaces are recorded in Table 1. Similar details of transition states are listed in Table 6.

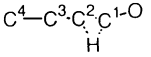
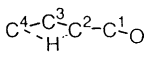
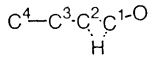
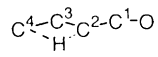
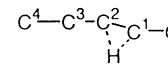
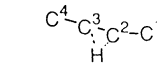
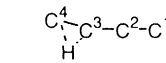
undertaken a theoretical investigation of the doublet neutral potential surface. Calculations are at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. The rearrangement mechanisms for the neutrals are similar to those already determined for the corresponding anions (Figs. 2 and 3). The reaction coordinate profile for the neutral rearrangement is shown in Fig. 5. Full details of neutral geometries and energies are listed in Table 1. Similar details of the transition states shown in Fig. 5 are contained in Table 6.

The data shown in Fig. 5 show that CCCCHO (**1**) requires an excess energy of at least 90 kJ mol$^{-1}$ to convert into CCCHCO (**2**) and an additional 60 kJ mol$^{-1}$ to rearrange further to HCCCCO (**4**). The rearrangements ***1*** → ***2*** and ***2*** → ***4*** are exothermic by 103 and 90 kJ mol$^{-1}$, respectively. These rearrangements are energetically feasible, provided the neutrals formed by vertical one-electron oxidation undergo further collision following the vertical oxidation. The excess energies required for rearrangement are within the energy range of other neutral rearrangements we have observed {e.g., CCCHO → HCCCO (134 kJ mol$^{-1}$) [26], linear $C_4$ to rhombic $C_4$ (120 kJ mol$^{-1}$) [27] and NCCCN → CNCCN (220 kJ mol$^{-1}$) [55]}. The alternative rearrangement through cyclic **5** (cf. Fig. 3) seems unlikely, since this species lies 148 kJ mol$^{-1}$ above **1** (Table 1), and we have not considered this possibility further.

### 3.5. The rearrangements of $[CCCCHO]^+$ and $[CCCHCO]^+$ to $[HCCCCO]^+$

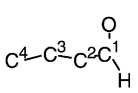
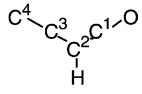
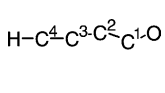
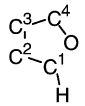
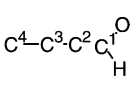
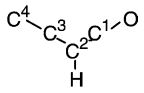
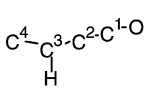
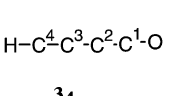
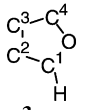
The $^-CR^+$ spectra of $[CCCCHO]^-$ and $[CCCHCO]^-$ show that the parent cations of these species rearrange to $[HCCCCO]^+$. Let us investigate these

Table 6
Energies and geometries of transition states shown in Figs. 5 and 6

| Neutral or cation |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| | TS $^{2}1/^{2}2$ | TS $^{2}2/^{2}4$ | TS $^{1}1^{+}/^{1}2^{+}$ | TS $^{1}2^{+}/^{1}4^{+}$ | TS $^{3}1^{+}/^{3}2^{+}$ | TS $^{3}2^{+}/^{3}3^{+}$ | TS $^{3}3^{+}/^{3}4^{+}$ |
| State | | | | | $^{3}A''$ | $^{3}A''$ | $^{3}A''$ |
| Symmetry | C1 | C1 | C1 | C1 | Cs | Cs | Cs |
| Energy (Hartrees)[a] | −227.38203 | −227.35915 | −227.03574 | −227.02871 | −227.01096 | −227.03015 | −227.03316 |
| Bond length (Å)[b] or angle (°)[b] | | | | | | | |
| $C^{1}C^{2}$ | 1.306 | 1.286 | 1.339 | 1.347 | 1.336 | 1.322 | 1.309 |
| $C^{2}C^{3}$ | 1.309 | 1.353 | 1.276 | 1.312 | 1.307 | 1.311 | 1.330 |
| $C^{3}C^{4}$ | 1.294 | 1.304 | 1.336 | 1.350 | 1.249 | 1.352 | 1.311 |
| $C^{1}O$ | 1.195 | 1.179 | 1.167 | 1.146 | 1.183 | 1.150 | 1.154 |
| $C^{1}H$ | 1.300 | | 1.332 | | 1.236 | | |
| $C^{2}H$ | 1.452 | 1.336 | 1.478 | 1.381 | 1.590 | 1.348 | |
| $C^{3}H$ | | | | | | 1.280 | 1.303 |
| $C^{4}H$ | | 2.128 | | 2.145 | | | 1.339 |
| $C^{1}C^{2}C^{3}$ | 176.5 | 170.9 | 175.8 | 153.2 | 165.9 | 174.0 | 179.1 |
| $C^{2}C^{3}C^{4}$ | 178.2 | 174.0 | 175.4 | 175.2 | 176.2 | 173.2 | 172.8 |
| $OC^{1}C^{2}$ | 167.3 | 174.3 | 167.0 | 168.6 | 159.6 | 177.0 | 180.0 |
| $HC^{1}C^{2}$ | 67.7 | | 67.2 | | 76.2 | | |
| $HC^{2}C^{3}$ | | 55.6 | | 55.8 | | 57.5 | |
| $HC^{3}C^{4}$ | | | | | | | 61.6 |
| $C^{1}C^{2}C^{3}C^{4}$ | −179.9 | 179.8 | 179.9 | 180.0 | 180.0 | 0.0 | 0.0 |
| $OC^{1}C^{2}C^{3}$ | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 0.0 |
| $HC^{1}C^{2}C^{3}$ | −0.1 | | 0.0 | | 0.0 | | |
| $HC^{2}C^{3}C^{4}$ | | −0.1 | | 0.0 | | 180.0 | |
| $HC^{3}C^{2}C^{1}$ | | | | | | | 180.0 |

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

Table 7
Energies and geometries of cations **1**–**5**

| Cation |  **$^1$1** |  **$^1$2** |  **$^1$4** |  **$^1$5** |  **$^3$1** |  **$^3$2** |  **$^3$3** |  **$^3$4** |  **$^3$5** |
|---|---|---|---|---|---|---|---|---|---|
| State | $^1$A′ | $^1$A′ | $^1$A′ | | $^3$A″ | $^3$A″ | $^3$A″ | $^3\Sigma$ | $^3$A″ |
| Symmetry | Cs | Cs | Cs | C1 | Cs | Cs | Cs | C*V | Cs |
| Energy (Hartrees)[a] | −227.08287 | −227.12930 | −227.14994 | −227.01679 | −227.02892 | −227.11549 | −227.07903 | −227.17070 | −227.01586 |
| Dipole moment (Debye)[b] | 2.85 | 3.02 | 4.33 | 2.10 | 2.48 | 1.73 | 2.47 | 4.12 | 1.42 |
| Bond length (Å)[b] or angle (°)[b] | | | | | | | | | |
| $C^1C^2$ | 1.488 | 1.430 | 1.335 | 1.381 | 1.367 | 1.3876 | 1.305 | 1.311 | 1.407 |
| $C^2C^3$ | 1.248 | 1.330 | 1.304 | 1.301 | 1.255 | 1.367 | 1.352 | 1.288 | 1.296 |
| $C^3C^4$ | 1.340 | 1.327 | 1.250 | 1.380 | 1.345 | 1.238 | 1.374 | 1.258 | 1.425 |
| $C^1O$ | 1.206 | 1.128 | 1.150 | 1.394 | 1.273 | 1.135 | 1.157 | 1.152 | 1.372 |
| $C^4O$ | | | | 1.353 | | | | | 1.340 |
| $C^1H$ | 1.096 | | | 1.083 | 1.109 | | | | 1.084 |
| $C^2H$ | | 1.094 | | | | 1.093 | | | |
| $C^3H$ | | | | | | | 1.11 | | |
| $C^4H$ | | | 1.077 | | | | | 1.077 | |
| $C^1C^2C^3$ | 166.7 | 114.4 | 147.0 | 125.6 | 177.9 | 119.5 | 176.5 | 180.0 | 114.3 |
| $C^2C^3C^4$ | 175.2 | 179.5 | 179.2 | 81.7 | 178.9 | 178.9 | 128.5 | 180.0 | 100.8 |
| $OC^1C^2$ | 109.9 | 177.0 | 170.2 | 98.4 | 125.3 | 179.2 | 178.9 | 180.0 | 106.1 |
| $HC^1C^2$ | 121.5 | | | 138.6 | 120.8 | | | | 135.4 |
| $HC^2C^3$ | | 128.0 | | | | 123.6 | | | |
| $HC^3C^4$ | | | | | | | 109.9 | | |
| $HC^4C^3$ | | | 177.0 | | | | | 180.0 | |
| $C^1C^2C^3C^4$ | 180.0 | 180.0 | 180.0 | −31.8 | 180.0 | 180.0 | 0.0 | 0.0 | 0.0 |
| $OC^1C^2C^3$ | 0.0 | 0.0 | 180.0 | 15.7 | 180.0 | 180.0 | 180.0 | 0.0 | 0.0 |
| $HC^1C^2C^3$ | 180.0 | | | 177.5 | 0.0 | | | | 180.0 |
| $HC^2C^3C^4$ | | 0.0 | | | | 0.0 | | | |
| $HC^3C^2C^1$ | | | | | | | 180.0 | | |
| $HC^4C^3C^2$ | | | 180.0 | | | | | 0.0 | |

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

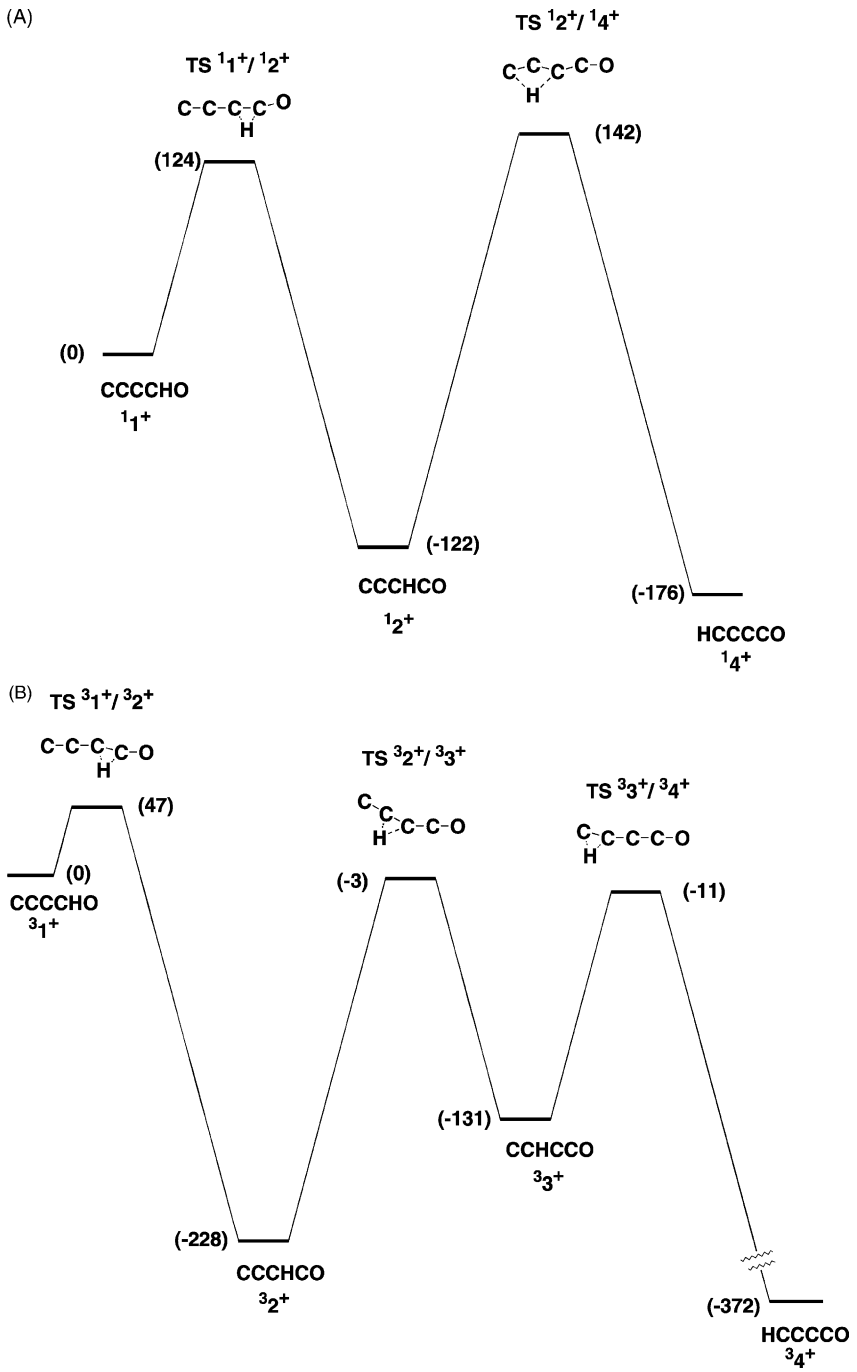



Fig. 6. Possible rearrangement pathways of (A) singlet and (B) triplet $[CCCCHO]^+$ and $[CCCHCO]^+$ to $[HCCCCO]^+$ involving H transfer. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Energies in kJ mol$^{-1}$ with that of $[CCCCHO]^+$ indicated as a nominal 0 kJ mol$^{-1}$ in each case. Full details of the geometries and energies of minima on the potential surfaces are recorded in Table 7. Similar details of transition states are listed in Table 6.

rearrangements in order to compare them with the neutral rearrangements shown in Fig. 5. There are singlet and triplet cation states of **1**, **2**, **4** and **5**. Cation **3** has only a stable triplet state. Full details of these are shown in Table 7. The singlet state is the ground state of $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{5}^+$ (by 142, 36 and 34 kJ mol$^{-1}$, respectively), but the ground state of $[HCCCCO]^+$ is the triplet by 55 kJ mol$^{-1}$. Only the triplet form of $[CCHCCO]^+$ is stable. We have not considered rearrangement by cyclisation of $[CCCCHO]^+$ to the cyclic cation $\mathbf{5}^+$ because of the high energy of the cyclic system (see Table 7).

Since we cannot control the energy of the collision processes which effect either the vertical $^-CR^+$ processes or the one-electron oxidation of a neutral to a cation, we must consider rearrangements on both singlet and triplet cation potential surfaces (even though the singlet of $[CCCCHO]^+$ ($\mathbf{1}^+$) is the ground state by 142 kJ mol$^{-1}$). The reaction coordinates for H rearrangements on the singlet and triplet potential surfaces are shown in Fig. 6A and B, respectively. Full details of transition states are recorded in Table 6. The triplet rearrangement (Fig. 6B) is the more facile of the two possibilities. This process involves sequential H rearrangement from one carbon to the next, passing through $^3\mathbf{2}^+$ and $^3\mathbf{3}^+$ before forming $^3\mathbf{4}^+$. The reaction has a maximum barrier (for step 1) of only 47 kJ mol$^{-1}$, and the overall process ($^3\mathbf{1}^+ \rightarrow {}^3\mathbf{4}^+$) is exothermic by 372 kJ mol$^{-1}$. The product $^3\mathbf{4}^+$ has a excess energy of 420 kJ mol$^{-1}$ as a consequence of the rearrangement shown in Fig. 6; this is sufficient to cause fragmentation of the cation (e.g., $^3[HCCCCO]^+ \rightarrow {}^3[HCCC]^+ + CO$; see Table 5). The singlet rearrangement (Fig. 6A) is not as energetically favourable as the triplet rearrangement. Even so, the singlet rearrangement compares favourably with cationic decomposition (see Table 5), since the maximum barrier shown in Fig. 6A is only 142 kJ mol$^{-1}$ and the reaction is exothermic by 176 kJ mol$^{-1}$. Thus, product $^1\mathbf{4}^+$ has an excess energy of 318 kJ mol$^{-1}$ (as a consequence of the rearrangement $^1\mathbf{1}^+ \rightarrow {}^1\mathbf{4}^+$): this energy is sufficient to cause decomposition of $^1\mathbf{4}^+$ (e.g., $^1[HCCCCO]^+ \rightarrow {}^1[HCCC]^+ + CO$; see Table 5).

## 4. Summary

This is the most complex NR study that we have undertaken to this time. First, the synthetic work to form two of the three anionic isomers was challenging; one of the isomers was formed by accident. Second, we had expected the "$C_4HO$" neutral system to show less rearrangement than the analogous "$C_3HO$" system that we studied earlier [26], because we thought that H rearrangements would become less feasible with an increase in the number of sequential H migrations [26]. Not only was this expectation not fulfilled, but (unwanted) rearrangements occurred for some of the precursor anions under the conditions required to effect $^-NR^+$ processes, in addition to the rearrangements of some neutrals and their corresponding cations. Only on one previous occasion have we faced a similar scenario (for the rearrangement of $[CC(O)(CN)]^-$ to $[NCCCO]^-$ [53]). Third, the experimental evidence was equivocal in key instances, for example, in determining whether rearrangement was occurring for certain neutral species. In these cases, the outcomes of the study rely exclusively on theory.

In conclusion:

1. The neutral doublet HCCCCO is stable for the microsecond duration of the NR experiment. The sequential vertical one-electron oxidations $[HCCCCO]^- \rightarrow HCCCCO \rightarrow [HCCCCO]^+$ occur with no change in HCCCCO connectivity.
2. The conversion of $[CCCHCO]^-$ to $[HCCCCO]^-$ has barriers for singlet and triplet rearrangements of 188 and 253 kJ mol$^{-1}$, respectively. A minority of $[CCCHCO]^-$ species might rearrange, but the majority should be stable under the conditions needed to effect conversion to CCCHCO. $^-CR^+$ experiments show that $[CCCHCO]^+$ rearranges completely to $[HCCCCO]^+$ either during or subsequent to the charge reversal process, and this is confirmed by theory. Theory also indicates that it is unlikely that CCCHCO will be stable for the duration of the NR experiment, and rearrangement to HCCCCO should occur.

3. A combination of experiment and theory indicates that if the cation $[CCCCHO]^+$ can be formed, it will rearrange to $[HCCCCO]^+$ via $[CCCHCO]^+$. Theory indicates that if neutral CCCCHO can be formed, then it is probable that it will be rearrange to HCCCCO through CCCHCO. The difficulty here is with the stability of anions $[CCCCHO]^-$. Theory shows that singlet anion $[CCCCHO]^-$ will rearrange to singlet $[CCCHCO]^-$ over a barrier of only $28\,kJ\,mol^{-1}$, but that further rearrangement to singlet $[HCCCCO]^-$ requires an extra $143\,kJ\,mol^{-1}$. In contrast, the conversion of triplet $[CCCCHO]^-$ to triplet $[CCCHCO]^-$ has a barrier of $211\,kJ\,mol^{-1}$. Such a reaction seems improbable, unless spin crossing to the singlet occurs. Since the difference in energy between singlet and triplet $[CCCCHO]^-$ is only $8\,kJ\,mol^{-1}$, significant proportions of each anion may be formed by the process shown in Eq. (1). It follows that some $[CCCCHO]^-$ ions may retain their structural integrity prior to or during CR and NR processes, but that others will rearrange, principally to $[CCCHCO]^-$. The situation concerning the CCCCHO system is therefore complex, with the possibility of rearrangement at each stage of the NR procedure.

## Acknowledgements

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