International Journal of Mass Spectrometry 195/196 (2000) 45–54

Conversion of neutral C_2COC_2 to C_4CO. Potential interstellar molecules

Suresh Dua, Stephen J. Blanksby, John H. Bowie*

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

Received 28 April 1999; accepted 30 August 1999

Abstract

Both $[C_4CO]^{-\cdot}$ and $[C_2COC_2]^{-\cdot}$ are formed in the ion source of a VG ZAB 2HF mass spectrometer by the respective processes $HO^- + Me_3Si–C{\equiv}C–C{\equiv}C–CO–CMe_3 \rightarrow [C_4CO]^{-\cdot} + Me_3SiOH + Me_3C^{\cdot}$, and $Me_3Si–C{\equiv}C–CO–C{\equiv}C–SiMe_3 + SF_6 + e \rightarrow [C_2COC_2]^{-\cdot} + 2Me_3SiF + SF_4$. The second synthetic pathway involves a double desilylation reaction similar to that first reported by Squires. The two radical anion isomers produce different and characteristic charge reversal spectra upon collisional activation. In contrast, following collision induced charge stripping, both radical anions produce neutral C_4CO as evidenced by the identical neutralisation reionisation ($^-NR^+$) spectra. The exclusive rearrangement of $C_2{}^{13}COC_2$ to $C_4{}^{13}CO$ indicates that $^{12}C–O$ bond formation is not involved in the reaction. Ab initio calculations (at the RCCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory) have been used to investigate the reaction coordinates on the potential surfaces for both singlet and triplet rearrangements of neutral C_2COC_2. Singlet C_2COC_2 is less stable than singlet C_4CO by 78.8 kcal mol^{-1} and requires only 8.5 kcal mol^{-1} of additional energy to effect conversion to C_4CO by a rearrangement sequence involving three C–C ring opening/cyclisation steps. (Int J Mass Spectrom 195/196 (2000) 45–54) © 2000 Elsevier Science B.V.

Keywords: Anions and neutrals; Isomers at C_5O

---

1. Introduction

Cumulenes and polycarbon monoxides have been detected in circumstellar envelopes [1–3] that surround red giant stars and dark interstellar molecular clouds [4]. 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 [1–4]. In contrast, there has been only limited detection of polycarbon monoxides. The linear species C_2O and C_3O have been detected toward the dark molecular cloud TMC-1 [5,6] whereas preliminary measurements suggest that C_5O may also be present, but this is yet to be confirmed [7]. A number of theoretical studies have been devoted to polycarbon monoxides [8–14]. The rotational spectra of C_nO ($n = 2–9$) have been detected in pyrolytic decomposition and pulsed discharge nozzle experiments [10–14]. In this article we (1) describe unequivocal syntheses of the isomers $[C_4CO]^{-\cdot}$ and $[C_2COC_2]^{-\cdot}$ and show that they are stable species, and (2) show that collision induced neutralisation of both $[C_4CO]^{-\cdot}$ and $[C_2COC_2]^{-\cdot}$ produce neutral C_4CO.

---

* Corresponding author. E-mail: jbowie@chemistry.adelaide.edu.au

Dedicated to the memory of an outstanding ion chemist, Robert R. Squires.

PII S1387-3806(99)00188-8

2. Experimental

2.1. Computational methods

Geometry optimisations were carried out with the Becke 3LYP method [15,16] using the 6-31G* basis set within the GAUSSIAN 94 [17] suite of programs. Stationary points were characterised as either minima (no imaginary frequencies) or transition states (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 the zero-point vibrational energies, which were then scaled by 0.9804 [18], and used as a zero-point energy correction for the electronic energies calculated at this and higher levels of theory. We have previously reported the success of the B3LYP method in predicting geometries of unsaturated carbon chain structures. It was demonstrated that this method produced optimized structures at a low computational cost and compared favourably with higher level calculations [19]. More accurate energies for the B3LYP geometries were determined with the partially restricted open shell coupled cluster method, RCCSD(T) [20–25], using the Dunning aug-cc-pVDZ basis set [26,27], with GAUSSIAN 94 [17]. Calculations were carried out using the Power Challenge Super Computer at the South Australian Super Computing Centre (Adelaide).

2.2. Mass spectrometric methods

Collision induced (CID), charge reversal (CR), and neutralisation reionisation (NR) spectra were measured using a two-sector reversed geometry VG ZAB 2HF spectrometer with two collision cells situated between the magnetic and electric sectors. This instrument and the typical experimental conditions of negative ion chemical ionization (NICI) have been described in detail elsewhere [19,28]. Spectra were generated in the following manner. Samples were introduced into the source via a heated septum inlet, producing a measured pressure of 5×10^{-6} Torr inside the source housing. Typical ionization conditions were source temperature, 200 °C; ionizing energy, 70 eV (tungsten filament); accelerating voltage, -7 kV. All slits were fully open in order to minimize mass discrimination effects due to energy resolution [29,30]. The reagent ions HO^- and F^- were generated by electron impact on H_2O and SF_6, respectively (H_2O introduced through the septum inlet, SF_6 through the gas inlet, to give an operating pressure inside the source housing of $\sim 5 \times 10^{-5}$ Torr, and thus an estimated pressure inside the ion source of close to 0.1 Torr). Negative ion chemical ionization of the sample was either effected by (1) desilylation of a neutral trimethylsilylated substrate using HO^-, cf. [31], or (2) double desilylation (with F^- from SF_6), using a method similar to that introduced by Squires and co-workers (using NF_3 or NF_3/F_2) [32]. Collision induced spectra were obtained by collision of the incident anions with argon in the first of two collision cells at a pressure typically around 10^{-7} Torr. Neutralisation of the anion beam in the first collision cell was achieved by collision with oxygen gas at a typical pressure of 5×10^{-6} Torr; this reduces the main beam to 80% of its initial value, producing essentially single collision conditions in the collision cell [33]. Residual ions were removed using the deflector electrode, with neutrals passing into the second cell where they were reionised to the corresponding cation under identical conditions to those used in the first cell. The spectra were collected by reversing the polarity of the electric sector voltage and scanning the sector voltage. CR spectra were measured under the same conditions as those used for NR spectra, except that the deflector electrode is grounded. Although this CR method does increase the likelihood of double collisions, it allows direct comparison between NR and CR spectra [34–37]. All spectra were repeated a minimum of three times in order to establish their reproducibility.

2.3. Synthetic procedures

Tert-butyl trimethylsilylbutadiyne ketone ($Me_3Si–C≡C–C≡C–CO–CMe_3$) was synthesised by the reaction [38] between bis-trimethylsilylbutadiyne and pivaloyl chloride in the presence of anhydrous aluminium chloride.

Bis-trimethylsilylethynyl ketone ($Me_3Si–C≡C–CO–C≡C–SiMe_3$) and bis-trimethylsilylethylyl ^{13}C-ketone [$Me_3Si–C≡C–^{13}CO–C≡C–SiMe_3$ (^{13}C = 99%)] were prepared by reported procedures [39,40].

3. Results and discussion

3.1. Syntheses and structures of two isomeric C_5O radical anions

The anion radical $[C_4CO]^{-\cdot}$ has been prepared by the synthetic procedure is shown in Eq. (1). The first step of the reaction involves use of the gas phase $S_N2(Si)$ reaction [31] to give the anion $^-C_4COCMe_3$, which is formed with excess energy in the chemical ionisation source of the ZAB 2HF instrument, and decomposes by loss of $Me_3C^{\cdot}$ to yield the required anion radical $[C_4CO]^{-\cdot}$. The isomer $[C_2COC_2]^{-\cdot}$ may be prepared from $Me_3SiC_2COC_2SiMe_3$ and SF_6, using a double desilylation approach analogous to that first reported by Squires and co-workers (using NF_3 or a mixture of NF_3 and F_2) [32]. We do not know the intimate mechanism of this reaction, but we propose that the overall reaction can be represented by either Eq. (2) or (3). In accord with the mechanism proposed by Squires [32], Reactions (2) and (3) involve two $S_N2(Si)$ displacement reactions with F^-. The second S_N2 process is preceded by electron transfer within an intermediate anion complex [32]. The difference between Reactions (2) and (3) is that the two fluoride anions originate from one and two SF_6 molecules, respectively

$$\begin{aligned}&HO^- + Me_3SiC≡C–C≡C–CO–CMe_3\\&\quad\rightarrow {}^-C≡C–C≡C–CO–CMe_3\\&\qquad + Me_3SiOH\ {}^-C≡C–C≡C–CO–CMe_3\\&\quad\rightarrow [C_4CO]^{-\cdot} + Me_3C^{\cdot} \qquad (1)\end{aligned}$$

$$\begin{aligned}&Me_3SiC≡C–CO–C≡CSiMe_3 + SF_6 + e\\&\quad\rightarrow [C_2COC_2]^{-\cdot} + 2Me_3SiF + SF_4 \qquad (2)\end{aligned}$$

Table 1
Spectra of $C_5O^{-\cdot}$ isomers and a ^{13}C labeled analogue

Ion	Spectrum type	Spectrum [*m/z* (relative abundance)]
$[C_2COC_2]^{-\cdot}$	CID	(76), 48(100)[a]
	CR	See Fig. 1A
	$^-NR^+$	76(85), 64(10), 60(12), 52(22), 48(100), 40(6), 36(52), 28(18), 24(26)
$[C_2{}^{13}COC_2]^{-\cdot}$	CID	(77), 48(100)
	CR	77(72), 65(20), 61(55), 53(89), 48(100), 41(7), 36(38), 29(6), 24(29)
	$^-NR^+$	77(75), 65(11), 61(15), 53(25), 48(100), 41(5), 36(52), 29(17), 24(39)
$[C_4CO]^{-\cdot}$	CID	76, 48(100)[b]
	CR	See Fig. 1B
	$^-NR^+$	76(90), 64(12), 60(15), 52(25), 48(100), 40(5), 36(51), 28(20), 24(24)

[a] Peak width at half height = 109.4 ± 0.5 V.
[b] Peak width at half height = 98.7 ± 0.5 V.

$$\begin{aligned}&Me_3SiC≡C–CO–C≡CSiMe_3 + 2SF_6 + e\\&\quad\rightarrow [C_2COC_2]^{-\cdot} + 2Me_3SiF + 2SF_5{}^{\cdot} \qquad (3)\end{aligned}$$

Despite the logic of these syntheses, further evidence is necessary to confirm the atom connectivities of the two product anion radicals. The convential collision induced negative ion mass spectra (Table 1) of both source formed isomers show only loss of carbon monoxide to yield $C_4^{-\cdot}$. Although these spectra are not particularly diagnostic, the peak widths at half height of the daughter peaks are different in the two spectra (see Table 1), suggesting that the precursor radical anions have different structures. Charge reversal spectra [41–43] have been used to distinguish between isomeric cumulene anions (see, e.g. [19]). This method can also be used for the two $[C_5O]^{-\cdot}$ isomers considered here. The CR spectra (Fig. 1) of the two radical anion isomers are distinct and diagnostic. The CR spectrum of $[C_2COC_2]^{-\cdot}$ (Fig. 1A) shows cation fragments corresponding to $C_2^{+\cdot}$ and others formed by the competitive losses of O and C_2 (base peak) from the parent radical cation. In contrast, the CR spectrum (Fig. 1B) of $[C_4CO]^{-\cdot}$ shows major losses of C and CO (base peak) with only minor formation of $C_2^{+\cdot}$.

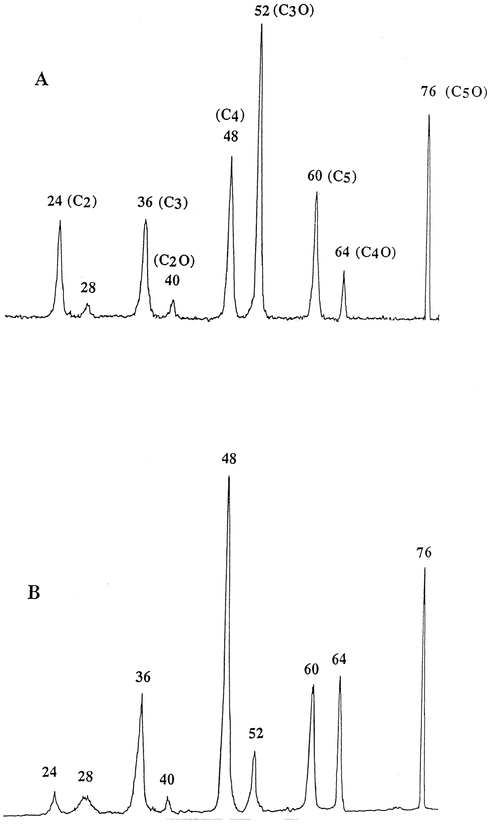


Fig. 1. CR spectra of (A) $[C_2COC_2]^{-\cdot}$ and (B) $[C_4CO]^{-\cdot}$. VG ZAB 2HF mass spectrometer—for operating details see Sec. 2.

The differences between the CI and CR spectra of the two anion radicals suggest that (1) there is no major interconversion between either the radical anion or radical cation isomers, and (2), there is structural continuity of each anion and cation pair, with favourable vertical Franck–Condon overlap linking each pair of potential surfaces [34–36].

Ab initio calculations [at the RCCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory] have been carried out for the radical anions and cations of C_4CO and C_2COC_2, and the results are summarised in Fig. 2. The 2Π ground state of the $[C_4CO]^{-\cdot}$ system is linear with $C_{\infty v}$ symmetry. All bond lengths are close to those expected for double bonds and the best valence bond representation is that of the cumulene oxide $[C{=}C{=}C{=}C{=}C{=}O]^{-\cdot}$. Linear $[C_4CO]^{-\cdot}$ has a computed dipole moment of 5.4 D. The $^2A'$ ground state of isomer $[C_2COC_2]^{-\cdot}$ is close to trigonal planar with C_s symmetry. The closest valence bond representation is $[(C{\equiv}C)_2C{=}O]^{-\cdot}$ but there are also minor contributions from the two degenerate contributors $[C{=}C{=}C(O){-}C{\equiv}C]^{-\cdot}$. The calculated dipole moment of this radical anion is 2.2 D and it is 41.0 kcal mol^{-1} less stable than linear $[C_4CO]^{-\cdot}$.

Data for the C_4CO and C_2COC_2 radical cations (Fig. 2) show that their structures are similar to those of the corresponding anions, in support of the experimental evidence that favourable vertical Franck–Condon overlap links each pair of anion/cation potential surfaces.

3.2. Charge stripping of $[C_4CO]^{-\cdot}$ and $[C_2COC_2]^{-\cdot}$

We have shown how the two isomeric C_5O radical anions are stable, and that there is favourable Franck–Condon overlap between anionic and cationic surfaces. What we now want to determine is whether it is possible to convert $[C_4CO]^{-\cdot}$ and $[C_2COC_2]^{-\cdot}$ to their analogous neutrals. This may be possible if there is favourable Franck–Condon overlap linking all three potential surfaces (radical anion, neutral and radical cation) for each structure [44].

The structures of neutral C_4CO and C_2COC_2 have been computed at the RCCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. The results are summarised in Fig. 3. There are structurally similar singlet and triplet cumulene oxide forms of C_4CO, with the singlet state ($^1\Sigma$) being the more stable by 56.6 kcal mol^{-1}. The singlet C=C=C=C=C=O has an estimated dipole moment of 1.68 D and an adiabatic electron affinity of 1.87 eV (43.1 kcal mol^{-1}) at this level of theory.

Neutral C_2COC_2 also has stable singlet and triplet structures, with the singlet structure being 23.1 kcal mol^{-1} more stable than the triplet state. The structures of the two neutrals are significantly different (see Fig. 3). The singlet state ($^1A'$) may be represented as a three membered ring with double bonds to each ring carbon. The estimated dipole moment of singlet C_2COC_2 is 1.54 D, the adiabatic electron affinity 3.5 eV (80.9 kcal mol^{-1}), and singlet C_2COC_2 is 78.8 kcal mol^{-1} less stable than singlet C_4CO at this level

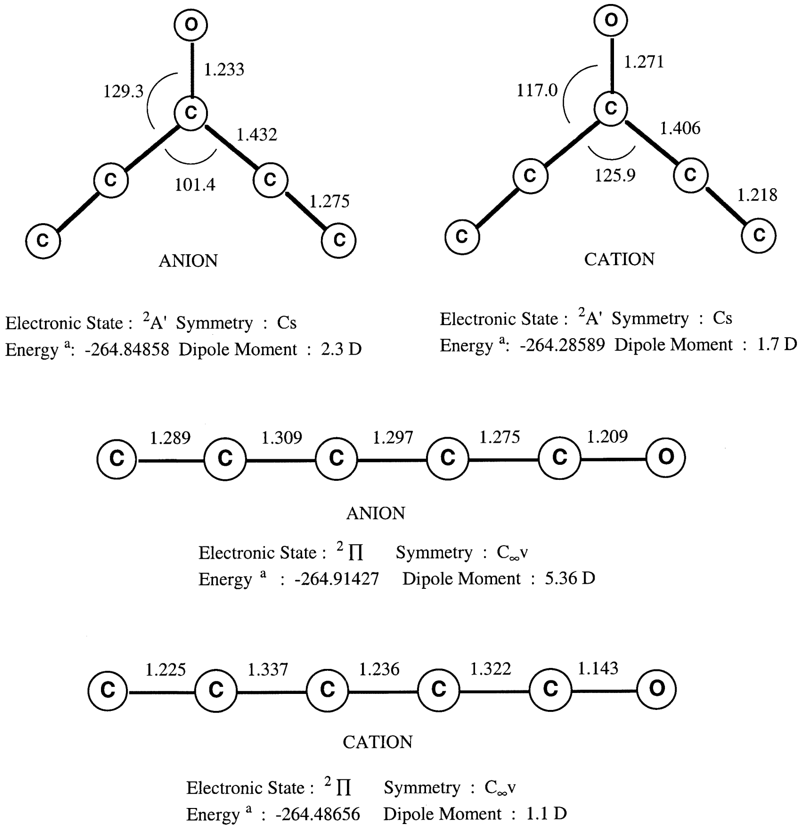


Fig. 2. Ab initio data for the radical anions and radical cations of C_2COC_2 and C_4CO. RCCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. ^{a}RCCSD(T)/aug-cc-pVDZ level of theory including zero point vibrational energy (calculated from vibrational frequencies at the B3LYP/6-31G* level of theory and scaled by 0.9804 [18]).

of theory. The triplet state ($^3A'$) looks more like the precursor anion: in this case the distance between C^2 and C^4 is 2.49 Å [cf. the C^2C^4 distance of 1.45 Å for the singlet ground state ($^1A'$)].

The neutralisation reionisation ($^-NR^+$) spectra of the two isomeric radical anions are recorded in Table 1. They are the same within experimental error, and very similar to the diagnostic CR spectrum of $[C_4CO]^{-\cdot}$ (Fig. 1B). This suggests that neutralision of both radical anion isomers leads to neutral C_4CO, and that rearrangement of C_2COC_2 to C_4CO must be complete within the timescale of the NR experiment ($\sim 10^{-6}$ s) [34–37]. In the case of the C_2COC_2 system, this must mean that vertical oxidation leads to energised C_2COC_2, which rearranges to the more stable C_4CO isomer.

The rearrangement of C_2COC_2 to C_4CO can only occur by several cyclisation/ring opening steps. These cyclisations may, in principle, involve either C–C and/or C–O bond formation. In order to differentiate between these possibilities we have synthesised the ^{13}C analogue $[C_2{}^{13}COC_2]^{-\cdot}$: the spectra of this labeled anion radical are recorded in Table 1. Both the CID and CR spectra show no scrambling of the ^{13}C label. This observation provides further support to the earlier conclusion that both the anion radicals and cation radicals are stable under the experimental conditions. However, neutralisation reionisation is the most important experiment because the $^-NR^+$ spectrum provides specific information concerning the mechanism of the neutral rearrangement C_2COC_2 to C_4CO. The base peak (*m/z* 48, $C_4^{+\cdot}$) of the $^-NR^+$

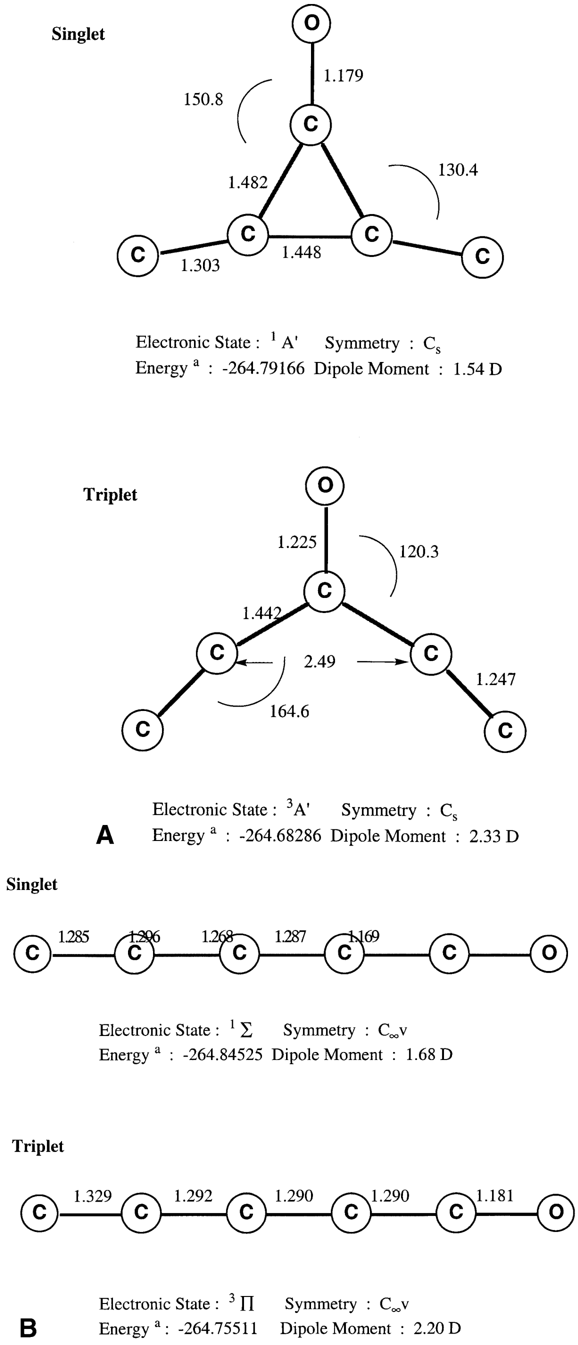


Fig. 3. Ab initio data for the neutrals C_4CO and C_2COC_2. RCCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory. ^{a}Same as in Fig. 2.

spectrum is formed by exclusive loss of ^{13}CO from the parent cation radical, whereas the peaks at *m/z* 36, 29, and 24 correspond to $^{12}C_3^{+\cdot}$, $^{13}CO^{+\cdot}$, and $^{12}C_2^{+\cdot}$, respectively. These data show that the rearrangement of $C_2{}^{13}COC_2$ proceeds specifically to $C_4{}^{13}CO$, which means that no ^{12}C–O bond formation occurs during this transformation.

3.3. *Rearrangement of C_2COC_2 to C_4CO: ab initio calculations*

The rearrangement of C_2COC_2 to C_4CO has been studied by ab initio methods using GAUSSIAN 94 at the B3LYP/6-31G* level of theory. Both singlet and triplet neutral states of C_2COC_2 may be formed from the C_2COC_2 radical anion (the two neutral states are 23.1 kcal mol^{-1} different in energy). Calculations indicate that the singlet and triplet states are formed with 41.4 and 12.5 kcal mol^{-1} of excess energy, respectively. This excess energy is the difference between the energies of the neutral ground state and that of the neutral at the anion surface. These calculated values assume that the precursor anion radical is not excited. If this is not the case, the excess energies of the singlet and triplet states will be greater than 41.4 and 12.5 kcal mol^{-1}, respectively. Because both singlet and triplet neutrals may be formed from the radical anion, and because both have excess energy, we must consider the probable rearrangement of both the singlet and triplet states of C_2COC_2 to C_4CO. Reaction coordinates of the two potential surfaces have been computed, but no consideration has been given to spin crossing from one surface to the other.

The mechanism of the singlet neutral rearrangement is summarised in Fig. 4 (geometries of the neutral C_5O isomers shown in Figs. 3 and 4 are the same, but the energies shown in Fig. 4 are computed at a lower level than those recorded in Fig. 3). The structures of intermediates **1** and **2**, and transition states **A**, **B**, and **C** shown in Fig. 4 are drawn in a simplified manner in order to aid visualisation of the course of the rearrangement. Full details of the geometries and energies of all intermediates and transition states shown in Fig. 4 are listed in Table 2.

The reaction proceeds from the singlet C_2COC_2 to singlet C_4CO via a three stage pathway. The rearrangement is initiated by lengthening of the C^2C^4

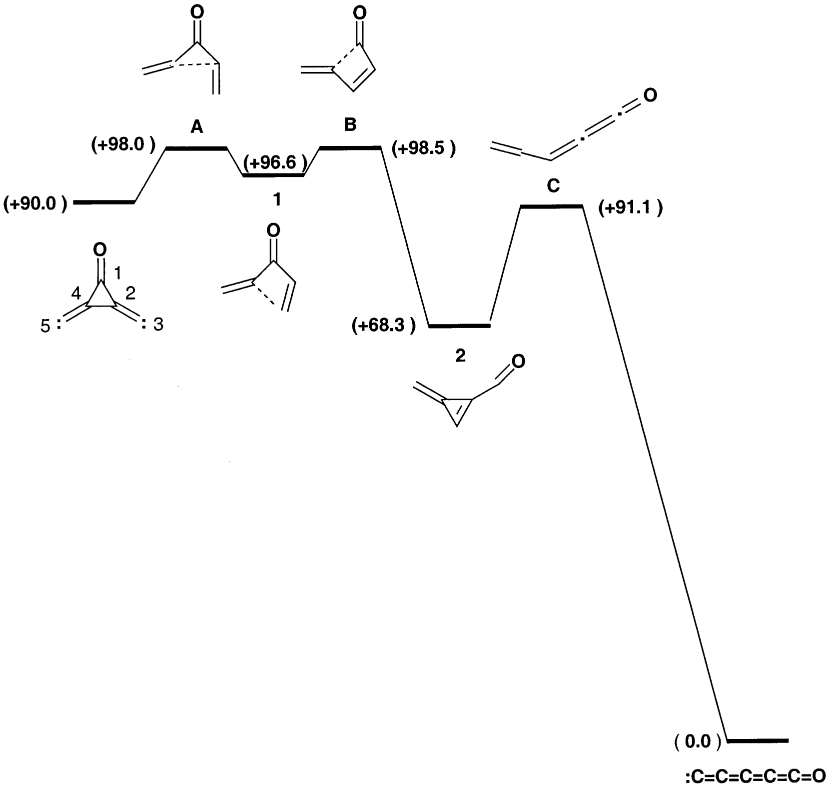


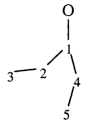
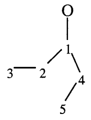
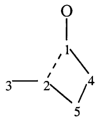
Fig. 4. The rearrangement of singlet C_2COC_2 to singlet C_4CO. Ab initio calculations at the B3LYB/6-31G* level of theory. Relative energies in kcal mol^{-1}.

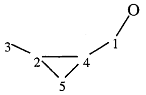
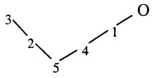
bond of C_2COC_2 (see Fig. 4 for numbering) with downward twisting of C^2C^3 (see transition state **A**), followed by partial formation of a bond between C^3 and C^4 to produce intermediate **1**. Bond formation between C^4 and C^3 and elongation of the C^4C^2 bond (through transition state **B**) is followed by reformation of a bond between C^2 and C^4 to yield intermediate **2**, concluded by C^2C^3 bond cleavage (through transition state **C**) to give the product C_4CO. The overall rearrangement is significantly exothermic [-90.0 kcal mol^{-1} at this level (B3LYP/6-31G*) of theory {-78.8 kcal mol^{-1} at the higher level [RCCD(T)/aug-cc-pVDZ] used for calculations recorded in Fig. 3)}, and requires only some 8.5 kcal mol^{-1} of excess energy to attain the highest energy transition state. Because the singlet neutral is formed with at least 41.4 kcal mol^{-1} of excess energy, this rearrangement process should be facile and singlet C_2COC_2 should not be detected following neutralisation of $[C_2COC_2]^{-\cdot}$.

The triplet neutral rearrangement is summarised in Fig. 5, with full details of transition state **D** listed in Table 3. The reaction coordinate of this rearrangement on the triplet surface is simpler than that (Fig. 4) of singlet C_2COC_2. The triplet neutral rearrangement proceeds via transition state **D** directly to triplet C_4CO, as confirmed by an IRC calculation on transition state **D**.

Comparison of the data contained in Figs. 3–5 indicate that the triplet neutral rearrangement requires more energy than the singlet neutral rearrangement. Not only does it require more energy to form triplet C_2COC_2 from the anion (the triplet is 23.1 kcal mol^{-1} more positive in energy than the singlet), but the triplet neutral has less excess energy (12.5 kcal mol^{-1} compared with 41.4 kcal mol^{-1} for the singlet), and

Table 2
Geometries and energies of intermediates and transition states in the singlet neutral rearrangement

	 Transition State **A**	 Intermediate **1**	 Transition State **B**
Electronic State		$^1A'$	
Symmetry	Cs	Cs	Cs
Energy (Hartrees)[a]	-265.37860	-265.38076	-265.38037
C_1O	1.18Å	1.17Å	1.17Å
C_1C_2	1.47Å	1.53Å	1.65Å
C_1C_4	1.42Å	1.43Å	1.39Å
C_2C_4	1.59Å	1.65Å	1.64Å
C_2C_3	1.30Å	1.30Å	1.30Å
C_4C_5	1.30Å	1.31Å	1.32Å
OC_1C_2	148.1°	149.0°	148.1°
$C_1C_2C_3$	149.8°	136.5°	124.1°
$C_4C_1C_2$	66.8°	67.6°	64.7°
$C_5C_4C_1$	98.2°	128.7°	129.9°

	 Intermediate **2**	 Transition State **C**
state	$^1A'$	
Symmetry	Cs	Cs
Energy (Hartrees)[a]	-265.427330	-265.3898506
C_1O	1.18Å	1.16Å
C_1C_4	1.43Å	1.30Å
C_4C_5	1.35Å	1.31Å
C_2C_4	1.44Å	2.00Å
C_2C_3	1.33Å	1.28Å
C_2C_5	1.50Å	1.41Å
OC_1C_4	136.8°	179.4°
$C_2C_5C_4$	61.2°	94.6°

[a] B3LYP/6-31G* level of theory including zero point vibrational energy (calculated from vibrational frequencies at the B3LYP/6-31G* level of theory and scaled by 0.9804 [18]).

the barrier to the first step of the triplet neutral rearrangement is 32.5 kcal mol^{-1} (compared with 8.5 kcal mol^{-1} for the first step of the singlet neutral rearrangement).

4. Summary and conclusions

Both the radical anions $[C_2COC_2]^{-\cdot}$ and $[C_4CO]^{-\cdot}$ have been synthesised and shown to be discrete and stable systems. Charge stripping of both radical anions leads to neutral C_4CO. All three potential surfaces of C_4CO are linked by favourable vertical Franck–Condon overlap. Neutral C_2COC_2 is energised during collision induced neutralisation of $[C_2COC_2]^{-\cdot}$ and the incipient neutral rearranges to the more stable isomer C_4CO in a strongly exothermic reaction. Both singlet and triplet states of C_2COC_2 can rearrange to C_4CO; energetically, the singlet rearrangement is the more favourable of the two processes.

We had hoped to make both of the neutrals

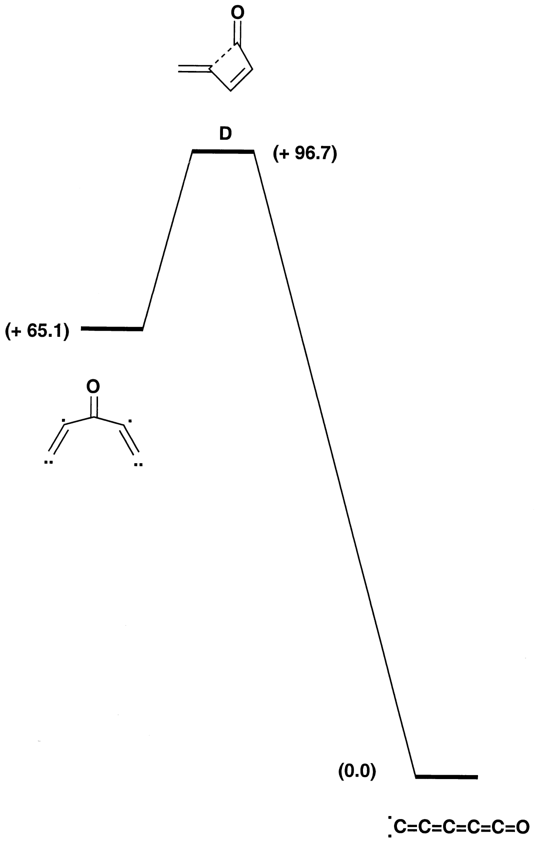
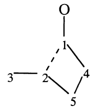


Fig. 5. The rearrangement of triplet C_2COC_2 to triplet C_4CO. Ab initio calculations at the B3LYB/6-31G* level of theory. Relative energies in kcal mol^{-1}. Product C_4CO is formed with excess energy, but not sufficient to affect decomposition to C_{4-} and CO [a process endothermic by 121.5 kcal mol^{-1} (D.W. Ewing, J. Am. Chem. Soc. 111 (1989) 8809)].

C_2COC_2 and C_4CO by charge stripping of precursor radical anions. Neutral C_4CO is almost certainly an interstellar molecule and we consider it possible that C_2COC_2 may be present in the same medium. We have succeeded in making C_4CO, but not the isomer C_2COC_2. Finally, the large dipole moments of $[C_4CO]^{-\cdot}$ and $[C_2COC_2]^{-\cdot}$ (5.4 D and 2.2 D, respectively) and the significant adiabatic electron affinities of the corresponding neutrals (1.9 and 3.5 eV, respectively) suggest the possibility that both of these radical anions may be detectable in the interstellar medium should their neutrals be present [45].

Table 3
Geometry and energy of transition state **D** in the triplet neutral rearrangement



	Transition State **D**
Symmetry	Cs
Energy (Hartrees)[a]	-265.27945
C_1O	1.18 Å
C_1C_2	1.62 Å
C_1C_4	1.39 Å
C_4C_5	1.31 Å
C_2C_4	1.65 Å
C_2C_3	1.30 Å
C_2C_5	1.58 Å
OC_1C_4	150.2 °
$C_2C_5C_4$	69.9 °

[a] B3LYP/6-31G* level of theory including zero point vibrational energy (calculated from vibrational frequencies at the B3LYP/6-31G* level of theory and scaled by 0.9804 [18]).

Acknowledgement

This project was financed by the Australian Research Council.

References

[1] H. Olofsson, in Molecules in the Stellar Environment, Lecture Notes in Physics, O.G. Jorgenson (Ed.), Springer, Heidelberg, 1994, pp. 114–133, and references cited therein.
[2] P.F. Bernath, K.H. Hinkle, J.J. Keady, Science 244 (1989) 562; K.H. Hinkle, in Molecules in the Stellar Environment, Lecture Notes in Physics, O.G. Jorgenson (Ed.), Springer, Heidelberg, 1994, pp. 99–114, and references cited therein.
[3] A. Omont, in Molecules in the Stellar Environment, Lecture Notes in Physics, O.G. Jorgenson (Ed.), Springer, Heidelberg, 1994, pp. 135–138, and references cited therein.
[4] D. Smith, P. Spanel, Mass Spectrom. Rev. 14 (1995) 255, and references cited therein.
[5] M. Ohishi, H. Suzuki, S. Ishikawa, C. Yamada, H. Kanamori, W.M. Irvine, R.D. Brown, P.D. Godfrey, N. Kaifu, Astrophys. J. 380 (1991) L39.
[6] H.E. Matthews, W.M. Irvine, P. Friberg, R.D. Brown, P.D. Godfrey, Nature 310 (1984) 125.
[7] B.E. Turner, in Chemistry and Spectroscopy of Interstellar Molecules, D.K. Bohme (Ed.), University of Tokyo Press, 1992, p. 75.
[8] R.D. Brown, D.A. McNaughton, K.G. Dyall, Chem. Phys. 119 (1988) 189.

[9] R.G.A.R. MacLagan, P. Sudkeaw, J. Chem. Soc. Faraday Trans. 89 (1993) 3325.
[10] M. Moazzen-Ahmalsi, F. Zerbetto, J. Chem. Phys. 103 (1995) 6343.
[11] P. Botschwina, J. Flügge, P. Sebald, J. Phys. Chem. 99 (1995) 9755.
[12] T. Ogata, Y. Ohshima, Y. Endo, J. Am. Chem. Soc. 117 (1995) 3593.
[13] R.D. Brown, F.W. Eastwood, P.S. Elmes, P.D. Godfrey, J. Am. Chem. Soc. 105 (1983) 6496.
[14] Y. Ohshima, Y. Endo, T. Ogata, J. Chem. Phys. 102 (1995) 1493.
[15] A.D. Becke, J. Phys. Chem. 98 (1993) 5648.
[16] P.J. Stevens, F.J. Devlin, C.F. Chablowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11 623.
[17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Peterson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzales, J.A. Pople, GAUSSIAN 94, Revision B.3, Gaussian Inc., Pittsburgh, PA, 1995.
[18] M.W. Wong, Chem. Phys. Lett. 256 (1996) 391.
[19] S.J. Blanksby, S. Dua, J.H. Bowie, D. Schröder, H. Schwarz, J. Phys. Chem. A 102 (1998) 9949.
[20] J. Cizek, Adv. Chem. Phys. 14 (1969) 35.
[21] J.A. Pople, R. Krishnan, H.B. Schlegel, J.S. Binkley, Int. J. Quantum Chem. 14 (1978) 545.
[22] C. Hampel, K. Peterson, H.-J. Werner, Chem. Phys. Lett. 190 (1992) 1.
[23] J.D. Watts, J. Gauss, R.J.J. Bartlett, Chem. Phys. 98 (1993) 8718.
[24] P.J. Knowles, C. Hampel, H.-J. Werner, J. Chem. Phys. 99 (1993) 5219.
[25] M.J.O. Deegan, P.J. Knowles, Chem. Phys. Lett. 227 (1994) 321.
[26] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.
[27] D.E. Woon, T.H. Dunning, J. Chem. Phys. 98 (1993) 1358.
[28] M.B. Stringer, J.H. Bowie, J.L. Holmes, J. Am. Chem. Soc. 106 (1984) 521.
[29] J.K. Terlouw, P.C. Burgers, J.L. Holmes, Org. Mass Spectrom. 14 (1979) 307.
[30] P.C. Burgers, J.L. Holmes, A.A. Mommers, J.E. Szulejko, J. Am. Chem. Soc. 106 (1984) 521.
[31] C.H. DePuy, V.M. Bierbaum, L.A. Flippin, J.J. Grabowski, G.K. King, R.J. Schmitt, S.A. Sullivan, J. Am. Chem. Soc. 102 (1980) 5012; G. Klass, V.C. Trenerry, J.C. Sheldon, J.H. Bowie, Aust. J. Chem. 34 (1981) 519.
[32] P.G. Wenthold, J. Hu, R.R. Squires, J. Am. Chem. Soc. 116 (1994) 6961.
[33] J.L. Holmes, Org. Mass Spectrom. 20 (1985) 169.
[34] G. Hornung, C.A. Schalley, M. Dieterle, D. Schröder, H. Schwarz, Chem. Eur. J. 3 (1997) 1866.
[35] C.A. Schalley, G. Hornung, D. Schröder, H. Schwarz, Int. J. Mass Spectrom. Ion Processes 172 (1998) 181.
[36] C.A. Schalley, G. Hornung, D. Schröder, H. Schwarz, Chem. Soc. Rev. 27 (1998) 91.
[37] C.A. Schalley, S.J. Blanksby, J.N. Harvey, D. Schröder, W. Zummack, J.H. Bowie, H. Schwarz, Eur. J. Org. Chem. (1998) 987.
[38] D.R.M. Walton, F. Waugh, J. Organomet. Chem. 37 (1972) 45.
[39] A.H. Albuts, H. Wyberg, J. Chem. Soc. Chem. Commun. (1988) 748.
[40] Y.Z. An, Y. Rubin, C. Schaller, S.W. McElvany, J. Org. Chem. 59 (1994) 2927.
[41] J.H. Bowie, T. Blumenthal, J. Am. Chem. Soc. 97 (1975) 2959.
[42] J.E. Szulejko, J.H. Bowie, I. Howe, J.H. Beynon, Int. J. Mass Spectrom. Ion. Phys. 13 (1980) 76.
[43] M. Bursey, Mass Spectrom. Rev. 9 (1990) 555.
[44] J.C. Lorquet, B. Leyh-Nihaut, F.W. McLafferty, Int. J. Mass Spectrom. Ion Processes 100 (1990) 465.
[45] See, e.g. S. Petrie, E. Herbst, Astrophys. J. 491 (1997) 210.