

Formation of neutral molecules of potential stellar interest by neutralisation of negative ions in a mass spectrometer

The application of experiment and molecular modelling in concert[☆]

John H. Bowie*, Salvatore Peppe, Suresh Dua, Stephen J. Blanksby¹

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

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Abstract

This paper is a modified version of a lecture which describes the synthesis, structure and reactivity of some neutral molecules of stellar significance. The neutrals are formed in the collision cell of a mass spectrometer following vertical Franck-Condon one electron oxidation of anions of known bond connectivity. Neutrals are characterised by conversion to positive ions and by extensive theoretical studies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6–31G(d) level of theory. Four systems are considered in detail, viz (i) the formation of linear C₄ and its conversion to the rhombus C₄, (ii) linear C₅ and the atom scrambling of this system when energised, (iii) the stable cumulene oxide CCCCCO, and (iv) the elusive species O₂C–CO. This paper is not intended to be a review of interstellar chemistry: examples are selected from our own work in this area.

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1. Introduction

The last decade has seen increasing interest in the chemistry of diffuse interstellar clouds and circumstellar envelopes, with some 120 molecules (Table 1) having been identified to this time [1–3]. The latter category has proved to be some of the richest extraterrestrial molecular sources. The expanding envelopes of gas and dust that surround carbon-rich, red giant stars contain a wide variety of carbon-based molecules. The best example is the carbon star IRC+10216, which is a source of more than 50 detected molecules [4]. The majority of stellar molecules have been detected by their rotational transitions using radio telescopes: thus there is a bias towards the detection of unsymmetrical molecules with significant dipole moments: as a consequence, many symmetrical molecules remain to be detected.

A number of methods have been used to form reactive neutrals of stellar significance in the laboratory, the most

popular involving laser ablation techniques coupled with spectroscopy (generally either microwave or infrared) to determine the bond connectivities of the products [5]. We have used a different approach to the synthesis of such molecules [3]. We first effect the synthesis of a charged precursor with known bond connectivity in the chemical ionisation source of our modified VG ZAB mass spectrometer. This is a four sector instrument (see Fig. 1), but we use only the first two sectors for the experiments described in this paper. The charged species is selected by the first magnet, it then proceeds to the first of the tandem collision cells positioned after the first magnet. This collision cell contains the inert gas argon. Collision of the ions with argon effects a number of reactions, including conversion of ions to the required neutral by a process assumed to involve vertical Franck-Condon one-electron oxidation (anion to neutral) or one-electron reduction (cation to neutral). Any ions produced in this cell are removed by a charged deflector plate positioned after the first cell. The required neutral then proceeds to the second collision cell, where it is ionised by oxygen (to produce positive ions from the neutral) or benzene (to form negative ions). This process is called neutralisation reionisation [6,7]. A schematic diagram of one-electron oxidation of a negative ion to neutrals followed by oxidation to cations is shown in Fig. 2. This is the procedure used for the examples

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

¹ Present address: Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, USA.

Table 1
Identified Interstellar and Circumstellar Molecules [1,2]

Number of atoms	Molecular species
Diatomic	H ₂ , HF, HCl, AlF, AlCl, C ₂ , CH, CN, CO, CP, CS, CSi, KCl, NH, NO, NS, NaCl, OH, PN, SO, SH, SiN, SiO, SiS,
Triatomic	C ₃ , C ₂ H, C ₂ O, C ₂ S, CH ₂ , HCN, HCO, H ₂ O, H ₂ S, HNC, HNO, MgCN, MgNC, N ₂ O, NaCN, OCS, SO ₂ , <i>cyc</i> -SiC ₂ , CO ₂ , NH ₂ , SiCN
Four atoms	<i>cyc</i> -C ₃ H, <i>l</i> -C ₃ H, C ₃ N, C ₃ O, C ₃ S, C ₂ H ₂ , HCCN, HNCO, HNCS, H ₂ CO, H ₂ CN, H ₂ CS, NH ₃ , SiC ₃
Five atoms	C ₅ , C ₄ H, C ₄ Si, <i>l</i> -C ₃ H ₂ , <i>cyc</i> -C ₃ H ₂ , CH ₂ CN, CH ₄ , HC ₂ CN, HC ₂ NC, HCOOH, H ₂ CHN, H ₂ C ₂ O, H ₂ NCN, HNC ₃ , SiH ₄
Six atoms	C ₅ H, C ₅ O, C ₂ H ₄ , CH ₃ CN, CH ₃ NC, CH ₃ OH, CH ₃ SH, HC ₂ CHO, HCONH ₂ , <i>l</i> -H ₂ C ₄ , C ₅ N
Seven atoms	C ₆ H, CH ₂ CHCN, CH ₃ C ₂ H, HC ₄ CN, HCOCH ₃ , NH ₂ CH ₃ , <i>cyc</i> -C ₂ H ₄ O
Eight atoms	CH ₃ C ₃ N, HCOOCH ₃ , CH ₃ COOH, C ₇ H, H ₂ C ₆ , CH ₂ OHCHO
Nine atoms	CH ₃ C ₄ H, CH ₃ CH ₂ CN, (CH ₃) ₂ O, CH ₃ CH ₂ OH, HC ₇ N, C ₈ H
Ten atoms	CH ₃ C ₅ N (?), (CH ₃) ₂ CO, NH ₂ CH ₂ COOH (?)
Eleven atoms	HC ₉ N
Thirteen atoms	HC ₁₁ N
Ions	H ₃ ⁺ , CH ⁺ , CO ⁺ , SO ⁺ , HCO ⁺ , HCS ⁺ , HOC ⁺ , N ₂ H ⁺ , CH ₂ D ⁺ (?), HCNH ⁺ , HOCO ⁺ , H ₃ O ⁺ , H ₂ COH ⁺ , HC ₃ NH ⁺

The question mark symbol (?) denotes uncertain detection.

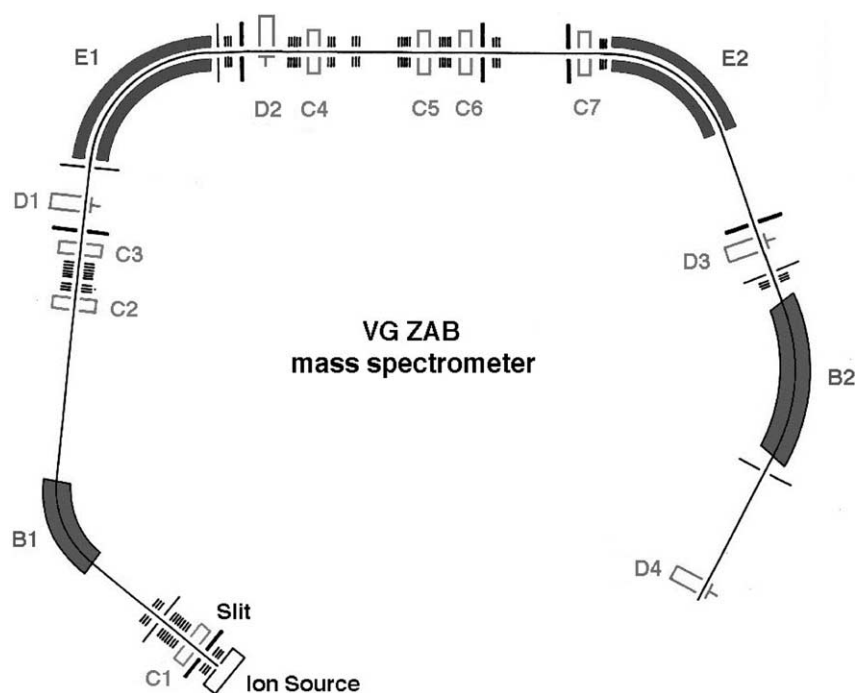


Fig. 1. Schematic diagram of the VG ZAB four sector instrument used for the studies reported in this paper. B, magnetic sector; C, collision cell; D, detector and E, electric sector. The tandem collision cells 2 and 3 were used for the experiments described in this paper.

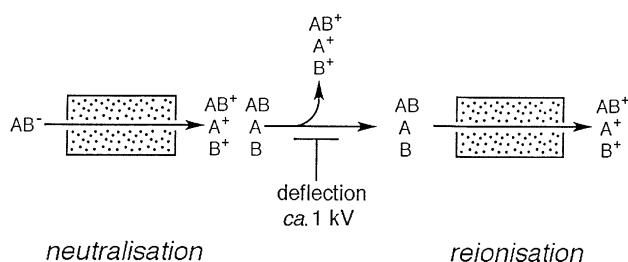


Fig. 2. Pictorial representation of a ⁻NR⁺ experiment.

described in this paper and is called a ⁻NR⁺ experiment (for the nomenclature of NR processes see [6]).

Some of the most interesting stellar molecules are the cumulenes (carbon clusters [8]) of formulae C_n, C_nH and C_nH₂ shown in Table 1 and the heterocumulenes derived from these (e.g. those containing O and N). Such cumulenes are formed on, or near dust particles (in interstellar dust clouds or circumstellar envelopes), by neutral or ion molecule reactions between elemental carbon and acetylene, and such products can react further by analogous reactions with acetylene or other neutrals [3]. Much of our effort in the past few years has been centred on the formation and

study of cumulenes, and we have reported the synthesis and structures of molecules with the following atomic compositions; C_4 [9], C_5 [10], C_5H [11], C_5H_2 [12], C_7H [13], and C_7H_2 [14]. The formation and rearrangements of linear C_4 and C_5 will be described as examples of this work.

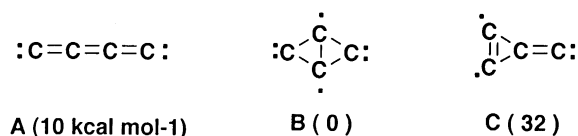
2. Discussion

2.1. Cumulenes

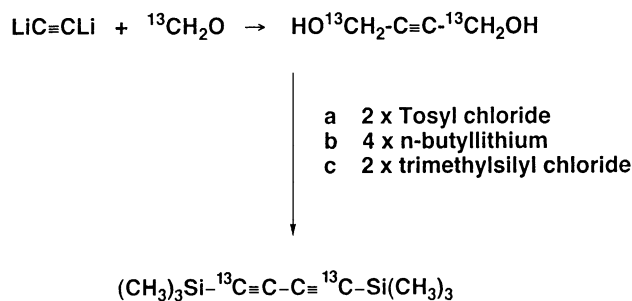
2.1.1. The linear and rhombus forms of C_4

The symmetrical cumulene C_4 has not, as yet, been detected as a stellar molecule, but the probability is that it will be in the near future. As early as 1977, it was proposed that the neutral ground state of C_4 might have a cyclic ground state [15]. Computational studies show that there are three low energy C_4 isomers; these are shown in Scheme 1, with the rhombus **B** being the lowest energy structure on the neutral surface at the CCSD(T)/aug-cc-pVDZ//B3LYP/6–31G(d) level of theory [9]. We wished to synthesise a linear C_4 neutral from an anion precursor of known bond connectivity, and to see whether the linear isomer **A** can isomerise to the more stable rhombus molecule **B**. We first made the doubly labelled ^{13}C precursor molecule $(CH_3)_3Si-^{13}C\equiv C-C\equiv^{13}C-Si(CH_3)_3$ (which has the appropriate bond connectivity) by the method outlined in Scheme 2.

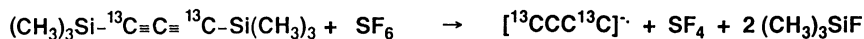
The precursor molecule is then introduced into the ion source of the mass spectrometer and allowed to react with the fluoride ion donor SF_6 by the S_N2 (Si) reaction (of the type



Scheme 1.



Scheme 2.



Scheme 3.

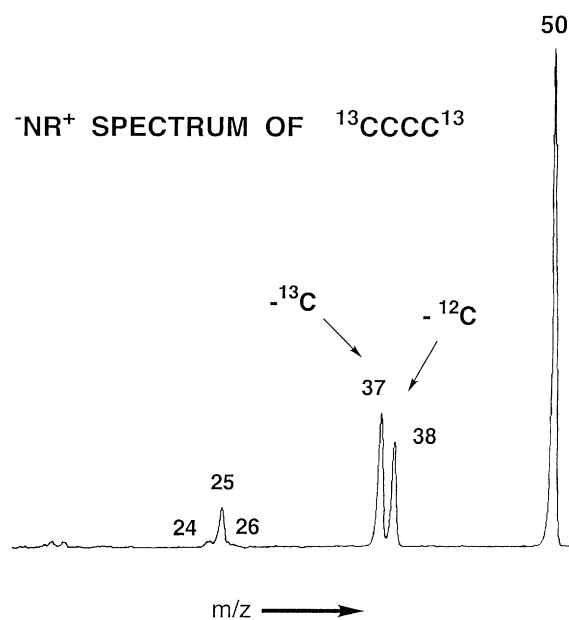


Fig. 3. The $^{-}NR^{+}$ spectrum of $[^{13}CCC^{13}C]^{-\bullet}$. Argon in first collision cell (transmission of main beam 90%). Dioxygen in second collision cell (transmission of main beam 80%).

first reported for gas-phase experiments by Squires [16]) to form the required radical anion $[^{13}CCC^{13}C]^{-\bullet}$. The overall reaction sequence is shown in Scheme 3.

The $^{-}NR^{+}$ spectrum of $[^{13}CCC^{13}C]^{-\bullet}$ is shown in Fig. 3. This spectrum is obtained by selecting the $^{13}CCC^{13}C$ radical anion beam with the magnet, allowing it to proceed into the first collision cell (see Fig. 2) where collision with argon may take place. The radical anion is converted into neutrals whose composite positive ion spectrum is produced by allowing the neutrals to proceed to the second collision cell where they are ionised by oxygen. Automatic scanning of the electric sector produces the positive ion spectrum shown in Fig. 3.

The first thing to notice in Fig. 3 is that there is a signal for parent $(^{13}C_2^{12}C_2)^{+\bullet}$. This means that the neutral is stable for the period (10^{-6} s) that it takes to go from the first to the second collision cell. Fragmentation of a neutral of structure $^{13}CCC^{13}C$ should only involve loss of the terminal ^{13}C atoms, whereas the $^{-}NR^{+}$ spectrum (Fig. 3) shows losses of both ^{12}C and ^{13}C . This indicates that the fragmenting neutral species are scrambling the atoms prior to or during fragmentation. We have shown independently that the radical cation (formed from the neutral) undergoes less atom scrambling than the neutral itself under the reaction conditions [9]. This experiment indicates that linear neutral C_4 is undergoing atom scrambling, but it gives no insight into the mechanism of scrambling.

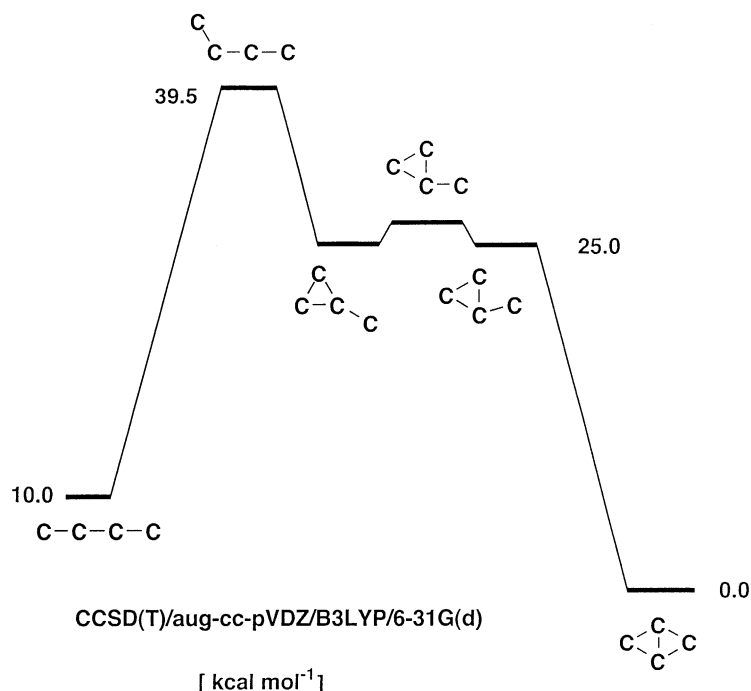
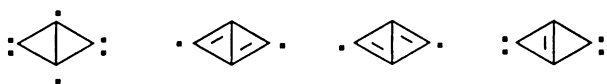


Fig. 4. The potential surface for triplet CCCC. CCSD(T)/aug-cc-pVDZ/B3LYP/6-31G(d) level of theory. Relative energies in kcal mol⁻¹. Structures show bond connectivities and geometries. Bond multiplicities are not indicated in this figure.



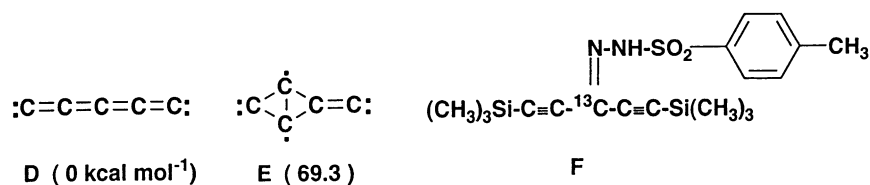
Scheme 4.

The results of theoretical calculations at the CCSD(T)/aug-cc-pVDZ/B3LYP/6-31G(d) level of theory for the potential surface of neutral C₄ are shown in Fig. 4. The data indicate that the scrambling must involve an equilibrium between linear C₄ and rhombus C₄. Thus this joint experimental and theoretical study suggests that rhombus C₄ is indeed a stable species. It also raises the question why the rhombus form should be more stable than the linear form. We do not know the answer to this question, but it of interest to consider the possible resonance structures shown in Scheme 4. Rhombus C₄ has five C–C bonds, each with a bond length of 1.46 Å, i.e. each bond has a bond order near 1.33.

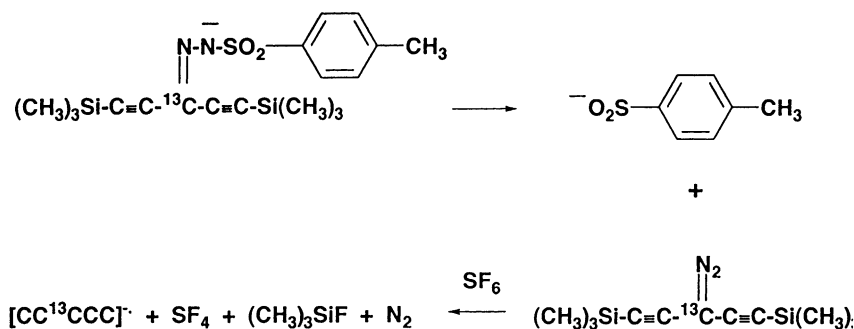
2.1.2. The linear cumulene C₅: does it undergo atom scrambling like C₄?

We have shown above that energised linear C₄ may rearrange to the more stable rhombus C₄. What will happen with the next homologue, linear C₅? Will it be a stable species, or will it scramble the atoms, and if so what is the scrambling mechanism? The linear C₅ molecule has been detected in star system IRC + 10216, [17] and has been the subject of a number of theoretical studies [8]. We have studied eleven isomers of C₅ at the CCSD(T)/aug-cc-pVDZ/B3LYP/6-31G(d) level of theory [10]. Of these, the singlet ground state linear CCCCC structure **D** (Scheme 5) is the most negative in energy, with the carbon substituted rhombus structure **E** being some 69 kcal mol⁻¹ more positive in energy than **D**.

We chose to synthesise the ¹³C labelled neutral, CC¹³CCC, for this study [10]. This synthesis is more complex than that of ¹³CCC¹³C. The precursor molecule synthesised was the sulfonyl hydrazone **F** (Scheme 5) which has the appropriate carbon atom connectivity. When this



Scheme 5.

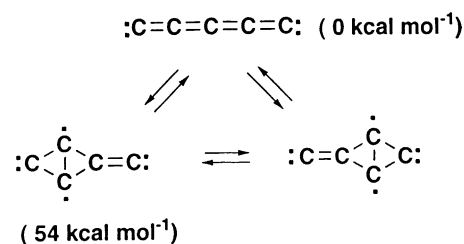


Scheme 6.

molecule is introduced in the ion source of the mass spectrometer together with HO^- (from water) the hydrazone unit is deprotonated, the sulfinyl anion $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$ cleaves off the hydrazone unit, and the double $\text{S}_{\text{N}}2(\text{Si})$ reaction removes the trimethyl silyl groups together with loss of N_2 as summarised in Scheme 6. The actual order of this sequence is not known: i.e. whether the double desilylation proceeds or is accompanied by the loss of N_2 . The overall process forms the required radical anion $[\text{CC}^{13}\text{CCC}]^{\cdot-}$.

The $^-\text{NR}^+$ spectrum of $[\text{CC}^{13}\text{CCC}]^{\cdot-}$ is shown in Fig. 5. If the carbon skeleton remains intact when CC^{13}CCC neutrals are energised, the only fragmentations noted in the $^-\text{NR}^+$ spectrum should be the competitive losses of ^{12}C and $^{12}\text{C}_2$. However, the spectrum exhibits losses of ^{12}C and ^{13}C together with $^{12}\text{C}_2$ and $^{12}\text{C}^{13}\text{C}$. Thus the atoms of the energised neutral are scrambling, just as they do for C_4 . We have shown by independent experiments that the carbon skeleton of radical anion $[\text{CC}^{13}\text{CCC}]^{\cdot-}$ remains intact during collisional activation, and that major scrambling of the atoms does not occur for the radical cation $[\text{CC}^{13}\text{CCC}]^{\cdot+}$ [10].

The potential surface for the rearrangement of linear C_5 is more complex than that of C_4 , but calculations show that the scrambling of singlet CCCCC involves rearrangement through two degenerate forms of a carbon substituted rhombus system. A simplified version of the process is summarised in Scheme 7.



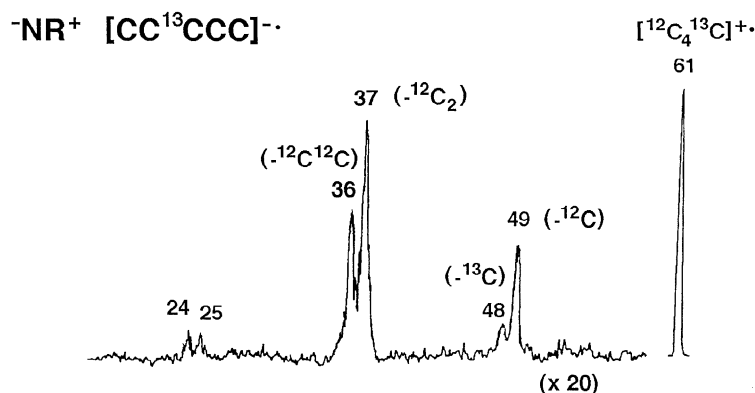
Scheme 7.

2.2. Cumulene oxides

We have synthesised a number of heterocumulenes: some of these are stellar molecules and others are related systems. We have studied the cumulene oxide systems C_3O , [18] HC_3O isomers, [19] C_5O isomers, [20] and C_7O [21]. We have also attempted to synthesise C_2O_2 [22] and O_2CCO [23]. The species C_5O and O_2CCO will be described to illustrate this work.

2.2.1. The interstellar molecule CCCCCO

The linear species C_2O and C_3O have been detected toward the dark molecular cloud TMC-1 [24,25]. Preliminary experiments suggest that C_5O is also present, but this has yet to be confirmed [26]. We have synthesised the precursor molecule **G** which has the correct bond connectivity for the formation of neutral CCCCCO in the mass spectrometer

Fig. 5. The $^-\text{NR}^+$ spectrum of $[\text{CC}^{13}\text{CCC}]^{\cdot-}$. Details as for Fig. 3.

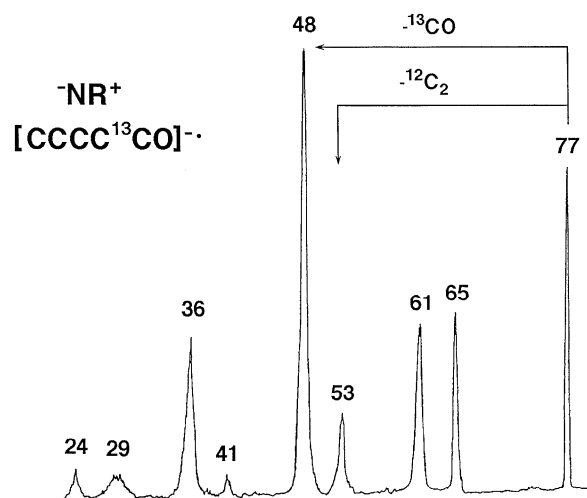
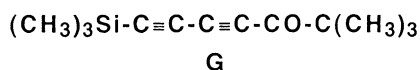
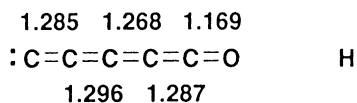


Fig. 6. The $^{-}\text{NR}^{+}$ spectrum of $[\text{CCCC}^{13}\text{CO}]^{-\bullet}$. Details as for Fig. 3.



[20]. Reaction of precursor molecule **G** in the ion source of the mass spectrometer with F^{-} (from SF_6) gives an anion species $^{-}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CO}-\text{C}(\text{CH}_3)_3$ which has excess energy and loses the *tert*-butyl radical to furnish radical anion $[\text{CCCCCO}]^{-\bullet}$. This species undergoes vertical one electron oxidation to form the linear cumulene oxide CCCCCO. The $^{-}\text{NR}^{+}$ spectrum of the labelled analogue $[\text{CCCC}^{13}\text{CO}]^{-\bullet}$ is shown in Fig. 6, and demonstrates (in contrast to the previous cases of C_4 and C_5) that no rearrangement of the C chain precedes or accompanies fragmentation. The reason for this is that neutral CCCCCO when energised undergoes loss of CO to furnish CCCC. An analogous process is not possible for C_4 and C_5 , which undergo the rearrangements described above.

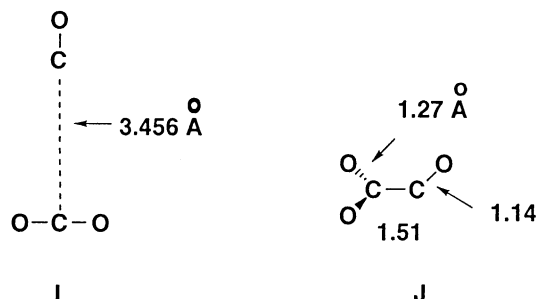
Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory indicate that C_5O has a linear singlet ground state with a dipole moment of 1.68D. That linear C_5O is a true cumulene oxide is evidenced by the calculated bond lengths (in Å) shown in structure **H** below.



2.3. The elusive molecule $\text{O}_2\text{C}-\text{CO}$

Carbon monoxide and carbon dioxide are components of interstellar dust clouds, circumstellar envelopes, and the earth's atmosphere. Is it possible that a stable molecule $\text{O}_2\text{C}-\text{CO}$ containing a covalent C–C bond can be formed from these two precursor molecules? It has already been demonstrated that the van der Waals complex **I** is formed between CO_2 and CO in a pulsed molecular beam using

diode laser spectroscopy with Fourier-transform microwave spectroscopy [27,28]. However this complex requires only $1.5 \text{ kcal mol}^{-1}$ to effect dissociation to CO and CO_2 , and thus will not be stable during a neutralisation–reionisation experiment.



Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory indicate that the triplet form of covalently bound $\text{O}_2\text{C}-\text{CO}$ should be a stable species [23]. The bond connectivities and bond lengths of this species are shown in structure **J**. The CO_2 and CO units are orthogonal to each other in this structure. In contrast, the singlet form of $\text{O}_2\text{C}-\text{CO}$ is an unstable species, decomposing in a reaction exothermic by $116 \text{ kcal mol}^{-1}$ to produce CO_2 and CO.

Our aim is to synthesise the radical anion corresponding to **J**, and to effect one-electron oxidation of this anion to triplet **J**. The geometries of the anion and neutral of **J** are very similar. A summary of calculations for this process together with the dissociation processes for triplet **J** are shown in Fig. 7. There are two major dissociation pathways. The first, which yields ^3CO and $^1\text{CO}_2$, is endothermic by 29 kcal mol^{-1} (at the level of theory used) and may not be accessible following oxidation of the radical anion. The second, which forms ^1CO and $^3\text{CO}_2$, is exothermic by $6.8 \text{ kcal mol}^{-1}$ but the process has a barrier of $5.4 \text{ kcal mol}^{-1}$. These calculations indicate that we should be able to detect triplet $\text{O}_2\text{C}-\text{CO}$ if it can be formed with less than 5.4 kcal of excess energy and if the lifetime of the neutral is $\geq 10^{-6} \text{ s}$.

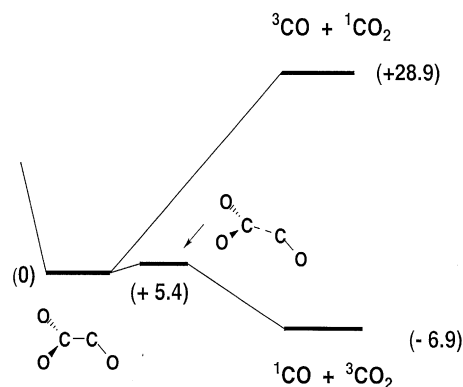


Fig. 7. Decomposition pathways of triplet neutral $\text{O}_2\text{C}-\text{CO}$. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kcal mol^{-1} .

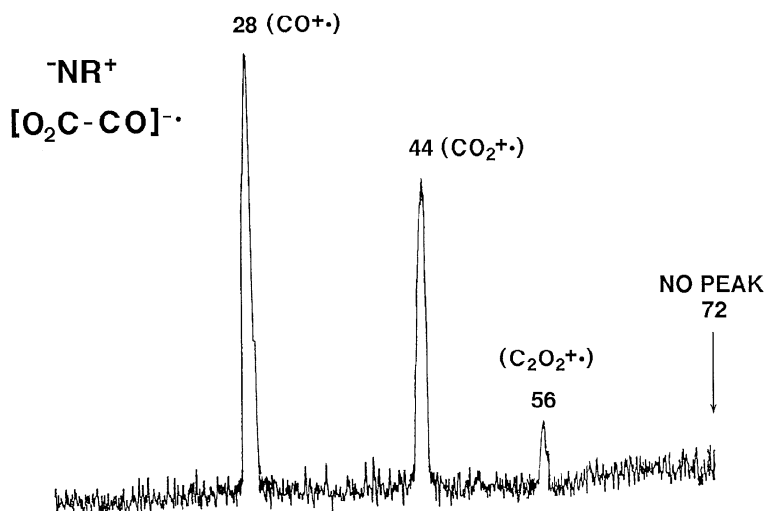
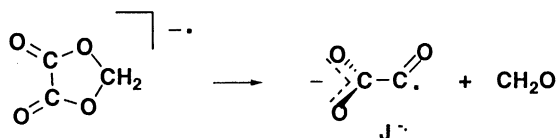


Fig. 8. The $^{-}\text{NR}^{+}$ spectrum of $[\text{O}_2\text{C}-\text{CO}]^{-\bullet}$. Details as for Fig. 3.

The radical anion of **J** can be synthesised by electron capture of 1,3-dioxolane-2,5-dione, followed by retro cleavage as shown in Scheme 8. The $^{-}\text{NR}^{+}$ spectrum of this anion is shown in Fig. 8. Neither this $^{-}\text{NR}^{+}$ spectrum nor the corresponding $^{-}\text{NR}^{-}$ spectrum (negative ion to neutral to negative ion) show recovery parent signals at m/z 72. This means either that triplet $\text{O}_2\text{C}-\text{CO}$ does not form under the conditions of this experiment, or that it does form but has a lifetime less than 10^{-6} s (the time between the formation of the neutral in the first collision cell and ionisation in the second collision cell) and thus cannot be detected in the NR experiment. The key experimental piece of evidence in distinguishing these two possibilities is forthcoming from an examination of Fig. 8. There is a minor peak at m/z 56 which corresponds to $[\text{OCCO}]^{+\bullet}$. We have studied the OCCO system in detail previously [22]. Neutral OCCO cannot be detected in a neutralisation experiment, thus the radical cation of OCCO (m/z 56) is unlikely to have originated from neutral OCCO. The only other possibility is that $[\text{OCCO}]^{+\bullet}$ comes from a decomposing $[\text{O}_2\text{C}-\text{CO}]^{+\bullet}$ radical cation (not detected in the $^{-}\text{NR}^{+}$ experiment), which in turn must have originated from a transient neutral $\text{O}_2\text{C}-\text{CO}$. We conclude that triplet $\text{O}_2\text{C}-\text{CO}$ is formed by one-electron oxidation of $[\text{O}_2\text{C}-\text{CO}]^{-\bullet}$, but that the lifetime of this elusive neutral must be less than 10^{-6} s under the conditions of the experiment.



Scheme 8.

3. Conclusions

We have shown that unusual cumulenes and cumulene oxides of stellar significance may be synthesised in a collision cell of a sector mass spectrometer by one-electron oxidation from precursor negative ions of known bond connectivity. Energised forms of some of these neutrals may undergo simple dissociation to form other neutral species. If a low-energy dissociation channel is not available, the energised neutral may undergo complex rearrangement reactions.

Acknowledgements

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