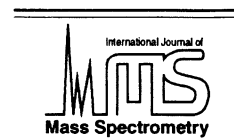




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Charge-stripping of anions in the gas phase: the formation of interesting neutrals and cations

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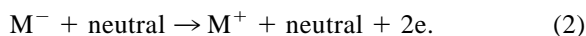
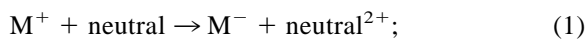
Abstract

This article traces the use of the charge-reversal and neutralization–reionization techniques of anions from the work done by Beynon and Cooks on charge-exchange reactions in the 1960s and 1970s to the recent use of neutralization/reionization for the study of interesting neutrals, including some of stellar significance. This article is not intended to be a review of the literature in these areas; much of the work cited has been done by members of my research group either alone or in collaboration with others. I apologize to those whose work has not been included; no slight is intended. (Int J Mass Spectrom 212 (2001) 249–265) © 2001 Elsevier Science B.V.

1. Charge-reversal of anions

This story commences in the early 1970s, following the seminal work of Beynon, Cooks, and colleagues, who used ion–molecule reactions in the field-free regions of a reverse sector mass spectrometer to effect charge-stripping [1–3] and charge-exchange reactions of ions [3–5]. We had commenced our work with organic negative ions at about the same time [6]. One of the problems with negative ions formed by either capture of a low-energy electron or by some chemical ionization process is that often the molecular radical anions or even-electron anions formed do not have sufficient energy to fragment. Fragmentation of these anions could at that time only

be induced using collisional activation of the anions [7]. Thus, we were particularly intrigued with the report of Keough, Beynon, and Cooks [5] that a positive ion could be converted into a negative ion by the collision process shown in Eq. (1). We wondered whether the opposite process could occur, that is, can a decomposing positive ion be produced from a precursor negative ion?



The questions were, first, can an organic negative ion be oxidatively charge-stripped to a positive ion, as shown in Eq. (2), and, second, if so, would some of the positive parent ions formed have sufficient internal energy to undergo characteristic fragmentations that might provide information concerning the structure of the initially non-decomposing negative ion? The instrument that Tom Blumenthal and I used for

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Dedicated to R. Graham Cooks to celebrate his sixtieth birthday and to honor his contributions to science—a colleague and friend for nearly 40 years.

these experiments was a Hitachi RMU 7D mass spectrometer of conventional double-sector design: an instrument that gave excellent formation of radical anions in the ion source, presumably because the source design assisted with the production of significant concentration of secondary electrons. The instrument was modified for automatic scanning of metastable and collision-induced peaks in the field-free region between the magnet and electric sector, using the metastable-defocusing technique [8]. Initially, we had no collision cell in the instrument—we just leaked air into the region of the spectrometer between the two analyzers. The formation of both parent and daughter positive ions from negative ions was spectacular: we called this technique the +E collision-induced mass spectrum of a negative ion [9,10] to be consistent with the earlier nomenclature of Cooks and Beynon for charge-exchange reactions [1–5]. By the mid-1980s it was called the charge-inversion, and then the charge-reversal (CR), technique [11,12], and finally, ${}^{-}\text{CR}^{+}$ [13,14]. Later, we converted the RMU 7D to reversed sector geometry by the method described by McLafferty [15] and inserted a homemade collision cell after the magnet so that we could obtain mass-analyzed charge-reversal ion kinetic-energy mass spectra. At that time we used N_2 or He as collision gas; more recently, we used Ar. Other collision gases have been used [13,14]: in particular, O_2 has been used to good effect. From 1985 onward, all of our negative-ion studies were carried out on a VG ZAB 2HF mass spectrometer, which has been much modified over the years.

The charge-reversal technique is now used routinely for several purposes: first, it can be used to form a variety of cations that cannot be formed by conventional ionization methods: early examples include RO^{+} [12,16,17] and RCO_2^{+} [12,18]; and, second, it can be used to provide structural information about the precursor negative ion provided that the parent cation does not undergo rearrangement before or during fragmentation: this was stressed early in our investigations [19]. The characteristic CR spectra of two isomers ($\text{CH}_3\text{CO}_2^{-}$ and ${}^{-}\text{OCH}_2\text{CHO}$; from [20]) are given in Fig. 1 to illustrate the applicability of the technique.

This oxidative conversion of an anion to a cation can be considered a vertical Franck-Condon process; that is, the cation initially formed has the same structure on the cation potential surface as that of the anion on its potential surface. If the potential well of the cation (on its potential surface) is directly above that of the anion (i.e., if the anion and the “stable” cation have the same or very similar geometries), then the parent cation will be produced with little excess energy by the vertical Franck-Condon collision process (see Fig. 2A). In contrast, if the stable cation and the precursor anion have significantly different geometries, then the cation will be formed with excess energy, as shown in Fig. 2B. Two things may then occur: either fragmentation of that cation occurs and no peak corresponding to the parent cation is observed, or the energized cation undergoes rearrangement to yield an isomer, which may fragment in a different manner than the initially formed cation (see [13,14] for recent discussions of vertical Franck-Condon processes). Two scenarios for CR processes are shown in Fig. 2. Rearrangement reactions do occur in CR spectra. Fortunately, they are the exception rather than the rule, and the method may be used (with the above caution noted) to give information concerning the structure of an anion. Charge-reversal spectra of negative ions generally show the same fragment ions that are observed in conventional electron-impact positive ion spectra, although the relative abundances of peaks are usually quite different in the two spectra. There are some interesting differences, however. For example, anions containing CH_2^{-} functionality (enolate ions RCOCH_2^{-} [21], allyl- CH_2^{-} , and aryl- CH_2^{-} ions, for example [22], ${}^{-}\text{CH}_2\text{SH}$ [23], etc.) show pronounced loss of CH_2 in the CR spectra; for example, see Fig. 3 for the CR spectra of CH_3S^{-} and ${}^{-}\text{CH}_2\text{SH}$ [23]. Losses of CH_2 in conventional positive ion spectra are quite rare.

Whenever possible, we use both the CR spectrum (positive-ion spectrum) of a negative ion and the collision-induced (CID) spectrum (negative-ion spectrum) of that negative ion when attempting to determine its structure by experiment. Using these two methods in concert constitutes a powerful analytical technique. We have used both methods extensively

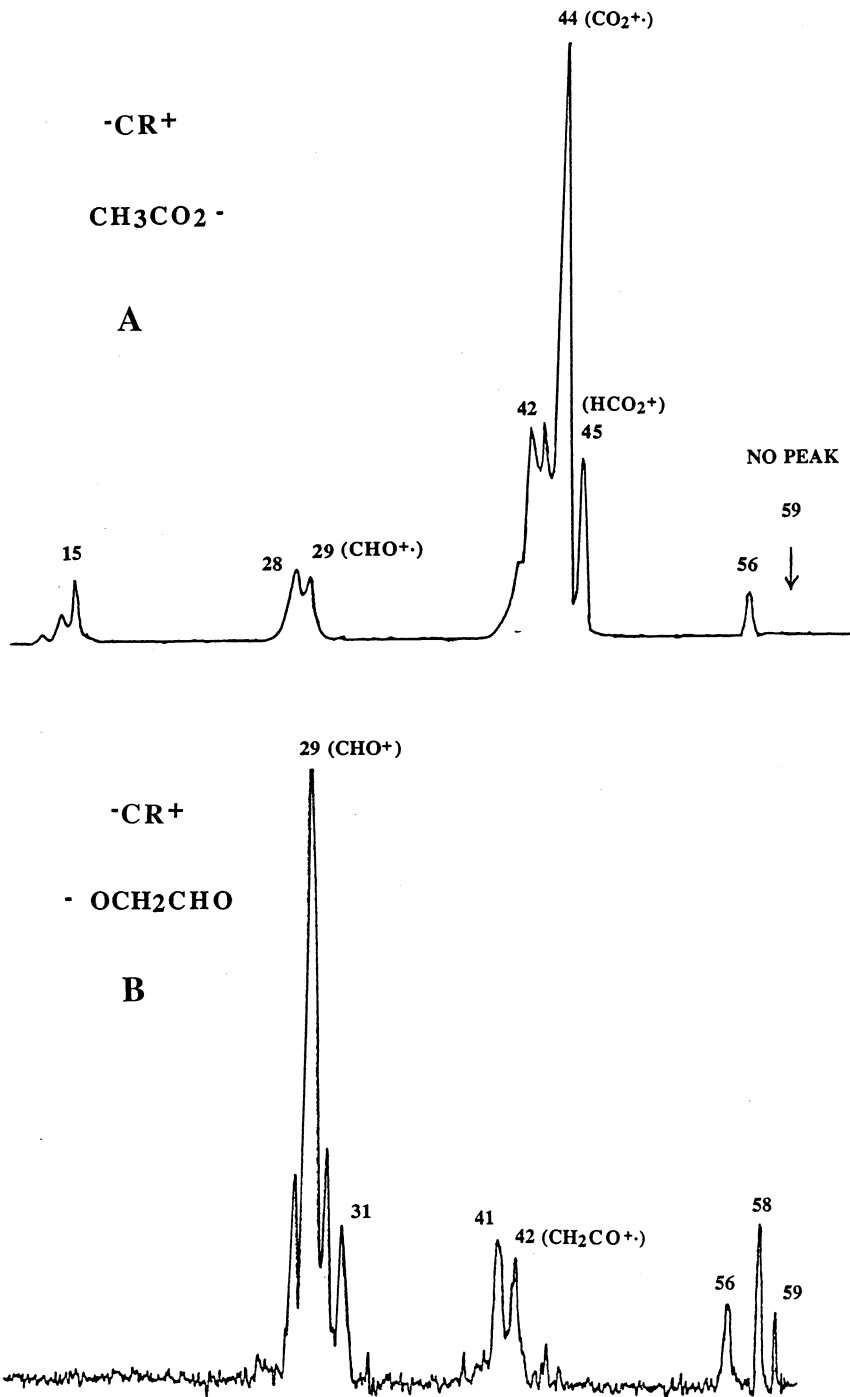


Fig. 1. $^{-}\text{CR}^{+}$ Spectra of $\text{CH}_3\text{CO}_2^{-}$ and $^{-}\text{OCH}_2\text{CHO}$, prepared, respectively, by the deprotonation of $\text{CH}_3\text{CO}_2\text{H}$ and HOCH_2CHO by HO^{-} in the ion source of a VG ZAB 2HF mass spectrometer. Ar in collision cell, pressure 5×10^{-7} mm Hg, equivalent to single collision conditions. Accelerating voltage -7000 V, magnet set to transmit appropriate parent negative ion, electric sector scanned automatically for positive ions [20].

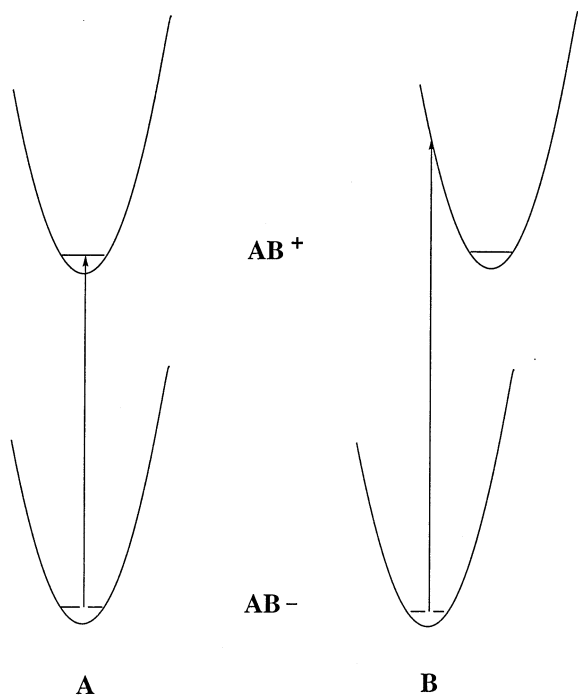


Fig. 2. Franck-Condon vertical oxidations for systems AB^- to AB^+ . In (A), the geometries of AB^- and AB^+ are the same. In this scenario, the $^-CR^+$ spectrum of AB^- will show parent positive ion AB^+ with no fragmentation. In (B), the geometry of the required AB^+ ion is significantly different from that of AB^- , so the potential well for AB^+ is displaced from that of AB^- . In this situation, energized AB^+ is formed. Depending on the extent of the excess energy of the cation and the thermochemistry of the various processes, a number of scenarios may pertain. The first is that the $^-CR^+$ spectrum will be that of AB^+ and contain peaks corresponding to (i) only fragment cations A^+ and B^+ (the scenario in [A]), (ii) both AB^+ together with A^+ and B^+ (the scenario in [B]). The second possibility is that energized AB^+ will rearrange to isomeric CD^+ and the $^-CR^+$ spectrum will show peaks corresponding to (i) only fragment ions C^+ and D^+ , or (ii) both CD^+ and the fragments C^+ and D^+ . The third possibility is that the $^-CR^+$ spectrum might be composite, showing some combination of AB^+ and CD^+ spectra.

for our studies of rearrangement reactions of even-electron anions (see [24] for a review and [25] for a particular example: the negative-ion pinacol rearrangement).

During our early work on the CR method, we assumed that the mechanism of the process involved the synchronous stripping of two electrons, as shown in Eq. (2). However, Holmes and Nibbering and their

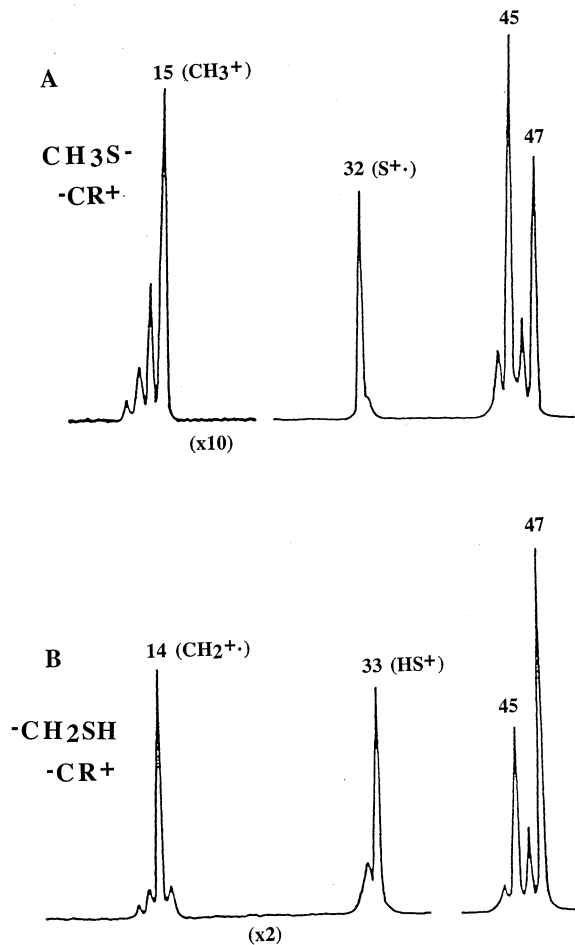


Fig. 3. $^-CR^+$ spectra of (A), CH_3S^- (from the S_N2 reaction between HO^- and $(CH_3)_2S$), and (B), $^-CH_2SH$ (by decarboxylation of $HSC_2CO_2^-$). VG ZAB 2HF mass spectrometer: conditions as described in Fig. 1 [23].

colleagues raised the question as to whether the charge-reversal process could be stepwise; that is, was the negative ion initially charge stripped to a neutral that subsequently, could be further charge stripped to a cation [26,27]? It is now clear that both of these processes can occur but that the charge-reversal process, in the majority of cases, does indeed involve synchronous stripping of two electrons. Even so, these questions of the possibility of a stepwise sequence of anion to neutral to cation lead to the neutralization/reionization technique.

2. Neutralization/Reionization of Negative Ions

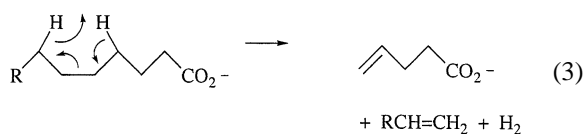
The discovery of methods of forming and detecting neutrals from ions in a mass spectrometer [28–41] is one of the more important advances in ion chemistry in the last 2 decades. Early on it was realized that this method could be used to generate unconventional neutrals from either cations or anions. The reaction between an ion and an inert gas in the first collision cell (in the field-free region following the magnet in a reverse-sector mass spectrometer) produces neutrals, both the neutral corresponding to the original parent ion and neutrals derived by fragmentation of the parent ion and/or neutrals. All residual ions are deflected in the region following the first collision cell, and a portion of the neutrals then pass into a second collision cell, where they are ionized to species whose mass spectra may be used as a probe for the formation of and structure of the neutrals. There are a number of variations of this technique. The procedure now called $^-NR^+$ (negative ion \rightarrow neutral \rightarrow positive ion; Ar often is the collision gas in the first cell, with O_2 in the second) is the principal method we will deal with in this article, but there are others, including $^-NR^-$, $^+NR^+$, and $^+NR^-$ (for a description of the nomenclature currently used for neutralization/reionization, see [13,14,33]). We entered this area after the technique had been developed by others [28–41]. We were interested in using it for two purposes: first, for assistance with the identification of the mechanism of an anion fragmentation by detecting the neutral(s) formed in that reaction, and second, in forming interesting neutrals from anions of known bond connectivities—in particular, transient molecules of stellar interest and related species.

3. Charge-remote fragmentations of even-electron negative ions

Mass spectrometry, in 2001, has reached a stage where the advances in new analytical techniques have outstripped a full understanding of the fundamental mechanisms of the fragmentation processes that make mass spectrometry one of the most important analyt-

ical techniques currently available for the structure determination of molecules.

It is essential that the fundamental chemistry behind ionic fragmentations and ion behavior be understood: we have spent the last 3 decades examining the behavior of radical anions produced by electron capture [42] and of even-electron anions formed by deprotonation of the original molecule [20,43]. After all that time, we have only scratched the surface of this important and fascinating area. We have proposed that the majority of fragmentations of even-electron negative ions are charge-directed processes, that is, that they are initiated from the anionic center in that molecule, and we have classified these processes [20,43]. It has also been proposed that some negative-ion cleavages are “charge remote,” that is, they occur at a distance from and uninfluenced by the charged center [44–46]. We were very skeptical initially about the concept of charge-remote processes of anions, but it is now clear that such reactions do occur: they occur principally when possible charge-directed reactions of a system are energetically unfavorable in comparison to the charge-remote processes.



It is sometimes very difficult to differentiate experimentally between a charge-directed reaction and a charge-remote reaction, even when using experiment and theory in concert. The classical charge-remote negative-ion process of Gross and Adams is shown for the long-chain systems shown in Eq. (3) [44–46] (this reaction also occurs for molecules where the anion and fragmenting centers are at different ends of steroidal type systems). However, what is to stop proton transfers along the carbon chain from forming various carbanions, one of which might initiate the loss of the elements of RC_2H_5 ? We have studied the system shown in Eq. (3), where R is $CH_2=CH$. Its CID mass spectrum is shown in Fig. 4 [47]. Atom labeling

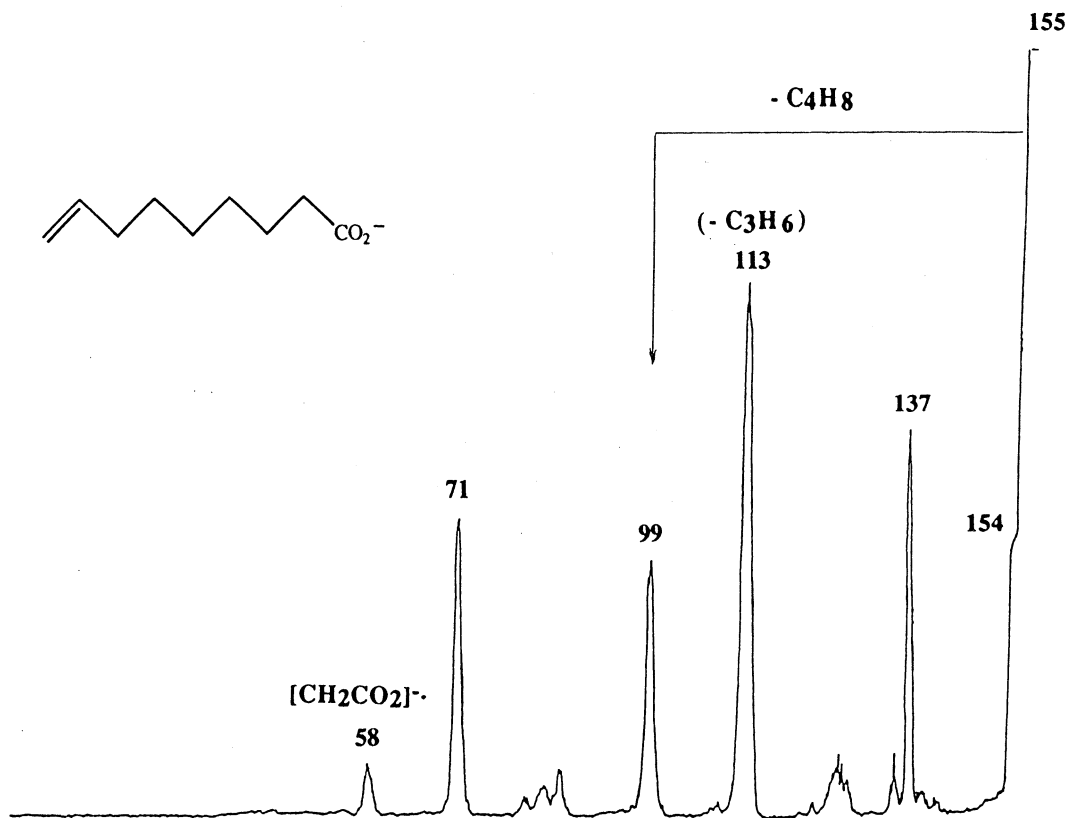
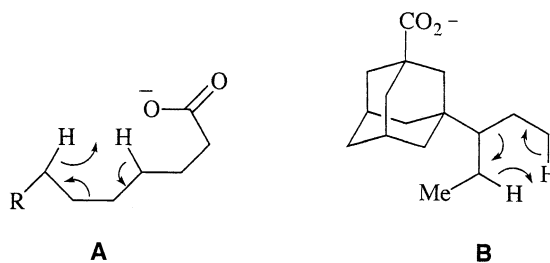


Fig. 4. CID mass spectrum of the non-1-enoate anion (formed by the reaction between DO^- and $\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{CO}_2\text{D}$). VG ZAB 2HF spectrometer, conditions as in Fig. 1, except that the electric sector is set to automatically scan negative ions [47].

(^2H and ^{13}C), together with theoretical calculations, supports the operation of the six-center process shown in Eq. (3) for loss of the elements of C_4H_8 ; this is a high-energy process with $\Delta\text{H} = +37 \text{ kcal mol}^{-1}$ and a barrier close to 88 kcal mol^{-1} (semi-empirical calculations at the AM1 level of theory).

In addition, this charge-remote process co-occurs with H (but not C) scrambling of the carbon backbone, together with other fragmentation processes that are charge initiated [47]. The key piece of circumstantial evidence to differentiate the two paradigms and to support the operation of this charge-remote process has been reported by Cordero and Wesdemiotis [48], who, in a ground-breaking study, first identified neutrals $\text{R}-\text{CH}=\text{CH}_2$ (rather than RCH_2CH_3) in the neutralization/reionization spectra of a number of the carboxylate anions studied earlier by Gross and Adams [44]. We

invited Chrys Wesdemiotis to study the neutrals formed from the nonenoate anion $[\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{CO}_2^-]$, and he confirmed the formation of butadiene, one of the two neutrals expected from this charge-remote process (cf. Eq. [3], R is $\text{CH}_2=\text{CH}$) [47].



There is still a problem with conformationally flexible systems of the type shown in Eq. (3). What is to stop

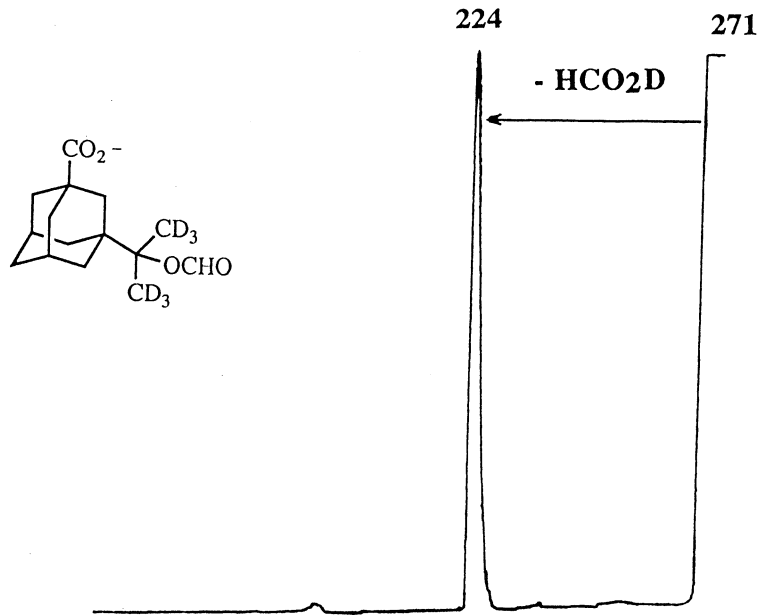


Fig. 5. CID mass spectrum. VG ZAB 2HF mass spectrometer. Conditions as in Fig. 4 [51].

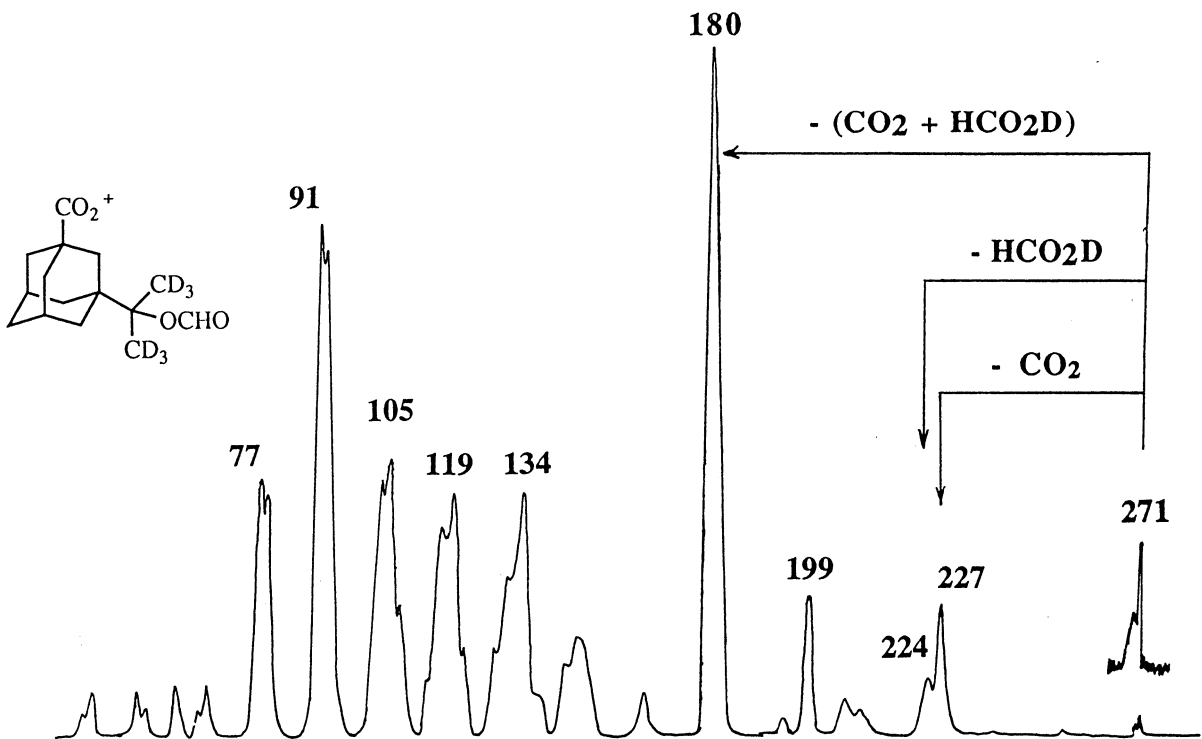
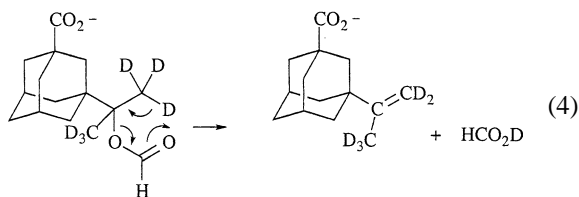


Fig. 6. ⁻CR⁺ mass spectrum. VG ZAB 2HF mass spectrometer. Conditions as for Fig. 1 [51].

participation of the carboxylate anion, as shown in **A** in the preceding scheme? If this occurs, then the reactions described above are not truly charge remote. We have been trying for some years to devise a simple system where the anion and reacting centers cannot approach each other through space, and the best model we have found to date is a rigid 1,3-disubstituted adamantane system where the anion is localized as a carboxylate. The syntheses of the neutral precursors are quite challenging. The carboxylate anion may be formed in the ion source of the mass spectrometer by reaction of a labeled carboxylic acid R–CO₂D with DO[−] or by the S_N2 reaction between a methyl ester R–CO₂Me and HO[−]. An appropriate model system built to investigate the Gross-Adams process is shown in **B** in the preceding scheme. The process shown in **B** (losses of C₂H₄ and H₂) does not occur. Processes that are observed are charge-remote radical losses from the side chain, including the loss of the whole side chain (loss of Et₂CH· from **B**) [49]. This may simply mean that we have chosen the wrong system to study; that is, the observed radical losses are more energetically favorable than the Gross-Adams reaction. Alternatively, the results may suggest that the Gross-Adams reaction shown in Eq. (3) really does require anchimeric assistance from the carboxylate anion (cf. **A**). This dilemma is unresolved. Further work is underway to find a more suitable model system for the study of the Gross-Adams reaction.



One charge-remote reaction that is definitely established using the 1,3-disubstituted adamantane approach is that shown in Eq. (4). This reaction is directly analogous to the thermal elimination of acetic acid from cyclohexyl acetate to yield cyclohexene [50], and shows similarities to both the Norrish II

photochemical rearrangement of ketones and the McLafferty rearrangement of radical cations [49,51]. This process is endothermic by only 10 kcal mol^{−1} [49,51], and the barrier has been calculated as ~53 kcal mol^{−1} (at the MP4 (SDTQ)/6-31G* level of theory) for the model system cyclohexyl acetate [52]. The neutralization/reionization (sometimes called neutral fragment/reionization because a study of this type involves characterization of a neutral products) spectrum of the carboxylate anion shows the presence of HCO₂D (*m/z* 47), thus providing further evidence for the operation of the charge-remote process shown in Eq. (4) [49]. The CID mass spectrum of the anion is shown in Fig. 5. This charge-remote reaction should also occur from the corresponding positive ion, provided, of course, there is no low-energy pathway that occurs in preference to the charge remote-reaction. In this case, the corresponding positive ion is available by charge reversal of the carboxylate anion. We were particularly fortunate with the choice of the model system in this case: the charge-reversal spectrum of the carboxylate anion is shown in Fig. 6 and clearly shows loss of HCO₂D. We are currently looking at other possible charge-remote reactions using the 1,3-disubstituted adamantane system, for example, retro Diels-Alder processes, Claisen and oxy Cope rearrangements, and so forth.

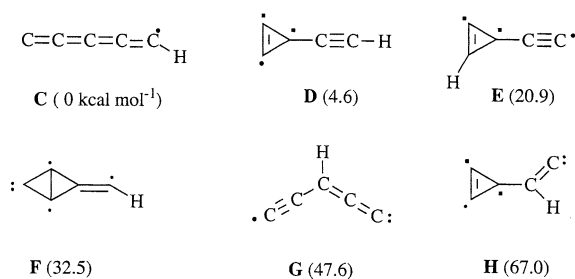
4. Stellar neutrals and related molecules

The last decade has seen an explosive growth in the detection of molecules in interstellar and circumstellar environs, using radio-telescopes principally (rotational spectroscopy) and, to a lesser extent, infrared telescopes [53]. Some 121 molecules have been detected to this time [54,55]. Of particular recent interest have been the cumulene (carbon cluster) hydrocarbon families C_n, C_nH, and C_nH₂, together with heterocumulenes, including C_nO, HC_nO, C_nN, HC_nN, C_nS, HC_nS, C_nSi, and HC_nSi [56]. These transient molecules are important both from a fundamental point of view (e.g., what are their structures and reactivities?) and because of their potential both as building blocks of larger carbon systems [57] and,

possibly, for forming precursors of peptides and nucleic acids. There are many methods for making these neutrals in the laboratory (see [56] and references cited therein). One of the most common methods is using laser ablation and related techniques. These techniques produce many interesting ions and molecules of initially unknown bond connectivity whose structures must be determined by spectroscopic techniques. In contrast, we wish to convert, in the mass spectrometer, anions of known bond connectivity to the corresponding neutrals and to characterize the neutrals by their positive ion mass spectra, that is, by ${}^{-}\text{NR}^{+}$.

The formation of transient neutrals as described earlier is by no means a trivial exercise. In summary, (i) the appropriate precursor molecule must be able to be synthesized in the laboratory by an unequivocal route, and often these precursors need to be tagged with heavy atoms (usually ${}^2\text{H}$ or ${}^{13}\text{C}$); (ii) this molecule must be able to be converted into the required precursor anion in the source of the mass spectrometer; (iii) this anion must not rearrange on collisional activation; viz. under similar conditions to those required to effect oxidative one-electron charge-stripping of the anion to the required neutral); (iv) the neutral should not have enough excess energy to allow it to rearrange to an isomer; and, (v) oxidative one-electron charge stripping of the neutral should give a positive ion that should give a spectrum characteristic of the previously formed neutral (i.e., the positive ion so formed must not rearrange to an isomer). (The ${}^{-}\text{NR}^{-}$ method has been used in some cases; for example, [58]. Unfortunately, the final negative-ion spectrum [derived from the neutral] is generally very weak even when the instrument is working at maximum sensitivity, and should only be used in a qualitative fashion.) Oxidative charge-stripping processes are presumed to occur by vertical Franck Condon processes (for recent reviews, see [13,14]) similar to those already previously described for the synchronous ${}^{-}\text{CR}^{+}$ process (cf. Fig. 2). It is surprising that all of these prerequisites could be successful for any system, but we will outline some where they appear to be so. The negative ion might rearrange during collision so that the method fails

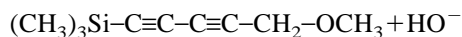
before the required neutral is formed (this is rare for the systems we have chosen to study: the only example to date is where $[\text{CC}(\text{O})(\text{CN})]^{-}$ rearranges to the more stable $(\text{OCCCN})^{-}$ [59]). Sometimes the final positive ion rearranges, constituting failure at the last step (e.g., for C_7O^{+} isomers [S. Dua, J.H. Bowie, unpublished observations]). Finally, the neutral may rearrange: this scenario has provided most interesting results, some of which are outlined below. To date, we have synthesized 25 transient molecules by this method: some have already been detected in interstellar or circumstellar environs, others are isomers of known stellar molecules, and others are related species. A number of examples are outlined below.

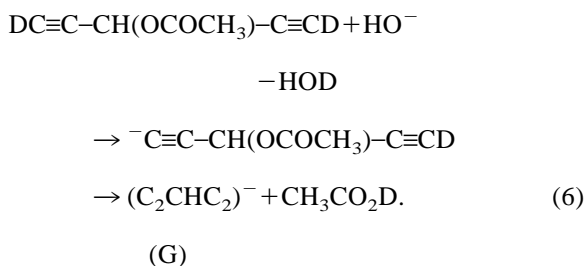
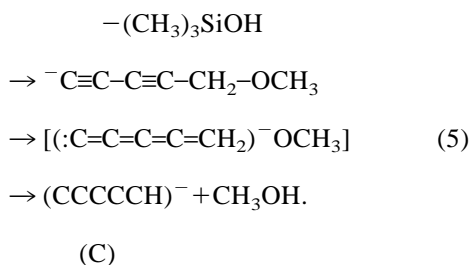


Scheme 1.

5. C_5H Neutral isomers and related systems

The odd carbon species C_3H and C_5H have been detected in circumstellar envelopes [60–63], with C_5H corresponding to the linear species **C** (Scheme 1). Theoretical calculations [64,65] indicate that there are six stable isomers of formula C_5H : these are shown in Scheme 1, with the relative energies shown calculated at the RCCSD(T)/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ level of theory [65]. The isomers **C** and **G** are accessible via their corresponding negative ions, which were prepared as shown in Eqs. (5) and (6). Anion **C** is formed by a standard sequence [66] initiated by an $\text{S}_{\text{N}}2$ (Si) reaction (cf. [67]), while the sequence to form the symmetrical anion **G** involves an interesting 1,3 elimination of $\text{CH}_3\text{CO}_2\text{D}$ [65].





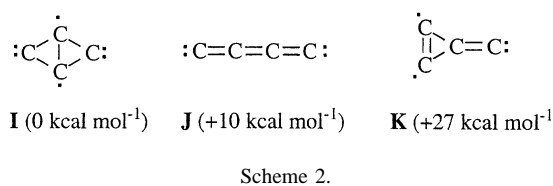
Potential surface calculations (at the level outlined previously) suggest that the bent neutral C_2CHC_2 should rearrange to the linear neutral C_4CH by two sequential 1,2 H transfers over a barrier (for the first and rate-determining step) of only 23 kcal mol^{-1} . We therefore expected, (i) the NR^+ spectra of the two isomers to be identical because of this probable rearrangement, and, (ii) even if two neutrals were stable, the positive ion spectra of these species might be identical as a consequence of possible atom scrambling within the respective positive ions before or during fragmentation. We were surprised when the NR^+ spectra of the two neutral isomers, although having some similar features, were reproducibly different (they are shown in Fig. 7).

The conclusion is if there is rearrangement of C_2CHC_2 to C_4CH during the neutral lifetime (10^{-6} s under the experimental conditions of the NR^+ experiment), then any such rearrangement is minimal. Thus, it appears that we have made both the C_4CH and C_2CHC_2 neutrals and that they are essentially stable under NR conditions, even though theory predicts that C_2CHC_2 could interconvert over a modest barrier to the more stable C_4CH . This neutralization must then form C_2CHC_2 neutrals with $< 23 \text{ kcal mol}^{-1}$ of excess energy. We have found that exactly similar scenarios pertain for several systems within the series C_nH_2 . For example, we have reported the

formation of three stable neutrals of formula C_5H_2 , viz. CCCCCH_2 , CCCHCCH , and HCCCCCH [68], and four stable neutral isomers of C_7H_2 , viz. $(\text{HCC})_2\text{CCC}$, HCCCCCCH , CCCCCCH_2 , and CCCH_2CCCC [69]. In the latter case, calculations at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory indicate that interconversion of the (“linear”) C_7H_2 isomers is unlikely because such isomerization requires a significant number of H transfers, and the barriers to some of these steps are within the range of $40\text{--}60 \text{ kcal mol}^{-1}$.

6. C_4 Isomers and related systems

The C_4 saga has been a controversial one since 1977, when it was first proposed that neutral C_4 may have a planar ground state [70]. Since then, tetracarbon has been the subject of intense study; although the elusive rhombus C_4 has been much studied theoretically, it has not been unequivocally identified experimentally. The many theoretical studies confirm that the rhombus C_4 (**I**, Scheme 2) and linear C_4 (**J**, Scheme 2) are close in energy, with, at best, the rhombic structure being the more stable by a few kilocalories per mol (e.g., see [71]). Our calculations, at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory, are summarized in Scheme 2. Singlet rhombus C_4 is the global minimum on the neutral potential surface, with the only other isomers within 50 kcal mol^{-1} of **I** being linear C_4 and the three-membered ring system **K** [58].



Neutral C_4 has not yet been identified as a stellar molecule, but the expectation is that it will be because linear C_4H and C_4H_2 are present in circumstellar envelopes together with linear C_5 and C_5H [55,56]. In collaboration with our colleagues Detlef Schröder and

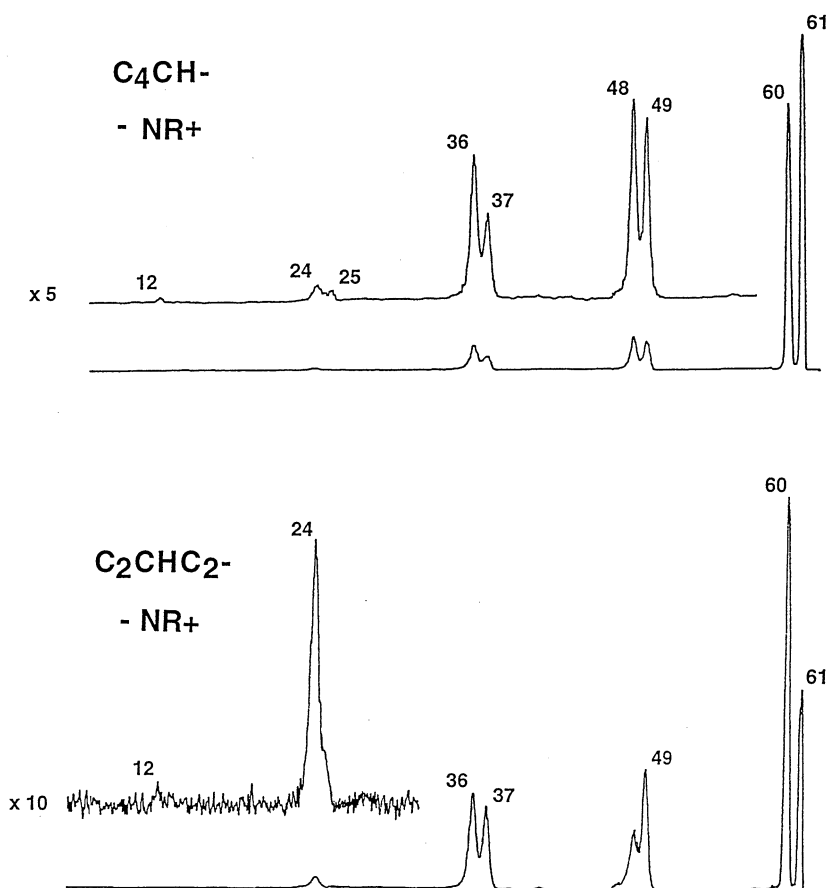
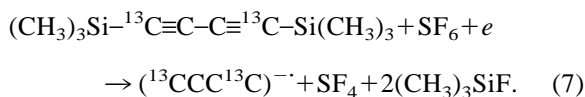


Fig. 7. $^{-}\text{NR}^{+}$ mass spectra of C_4CH^{-} and $\text{C}_2\text{CHC}_2^{-}$. VG ZAB 2HF mass spectrometer. Conditions as in Fig 1. except O_2 in collision cell 1 (pressure 1×10^{-6} mm Hg, 20% reduction in main beam signal), ion deflector after collision cell 1 turned on, O_2 collision cell 2 (pressure 1×10^{-6} mm Hg, 20% reduction in main beam signal) [66].

Helmut Schwarz, we set out to synthesize the linear C_4 radical anion and to ascertain whether following oxidative charge-stripping, the linear C_4 neutral rearranges to the rhombus C_4 . We synthesized the double-labeled species shown in Eq. (7) and, following bis-desilylation (using the SF_6 modification of the F^{-}/NF_3 method of Squires [72]), we formed linear $(^{13}\text{CCC}^{13}\text{C})^{-}$ in the ion source of the mass spectrometer. The order and precise mechanism of this sequence is not known, but overall, it may be represented as follows:



The CID mass spectrum (negative ion spectrum) of $(^{13}\text{CCC}^{13}\text{C})^{-}$ shows only one fragmentation: loss of a terminal ^{13}C atom. Thus, the linear anion does not rearrange under the conditions to be used for the neutralization experiment. The $^{-}\text{NR}^{+}$ and $^{-}\text{CR}^{+}$ spectra of $(^{13}\text{CCC}^{13}\text{C})^{-}$ are complex. However, both spectra show competitive losses of ^{12}C and ^{13}C with the loss ratio ($^{-12}\text{C} : ^{-13}\text{C}$) being larger in the $^{-}\text{NR}^{+}$ spectrum. These data show that there is atom scrambling taking place in both neutral C_4 and cation C_4 , with the scrambling more pronounced for the neutral. This was confirmed by a $^{-}\text{NR}^{-}$ experiment. We mentioned earlier that the CID spectrum of

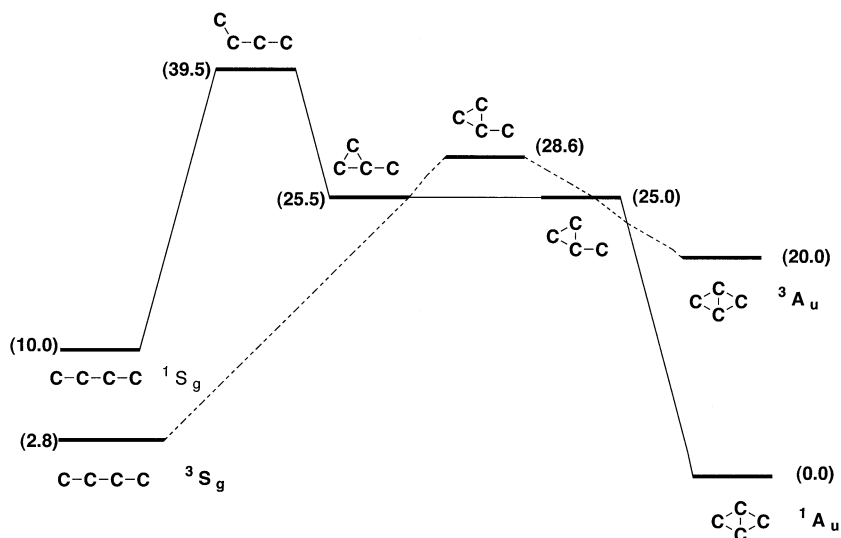


Fig. 8. Summary of theoretical calculations for the rearrangement of linear C_4 to rhombic C_4 . Continuous line for rearrangement of singlet. Dotted line for rearrangement of triplet. Relative energies are in kilocalories per mol. Energies calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Bond connectivities and geometries (not bond orders) given for all species shown [58].

$(^{13}CCC^{13}C)^{\cdot -}$ shows only loss of ^{13}C . When the anion is converted to the neutral and the neutral reconverted to an anion (using benzene as reagent gas in the appropriate collision cell), the $^{-}NR^{\cdot -}$ spectrum, although weak, shows a pronounced parent peak (recovery signal) together with two fragment peaks formed by the losses of both ^{12}C and ^{13}C from the parent radical anion. The loss ratio is close to 1 : 1. Thus, linear neutral C_4 scrambles its carbon atoms during its lifetime (10^{-6} s) in the $^{-}NR^{\cdot -}$ experiment. These experiments suggest that neutral C_4 is rearranging through a symmetrical intermediate: they do not, however, give information concerning the structure of that symmetrical intermediate.

Theoretical calculations have been carried out to rationalize this rearrangement and are summarized in Fig. 8. There are singlet and triplet forms of C_4 that are very similar in geometry and are only 7.2 kcal mol $^{-1}$ apart in energy. The triplet is the ground state. Vertical Franck-Condon oxidation will produce both singlet and triplet, and thus, possible rearrangement of each needs to be considered. Both are shown in Fig. 8: the singlet rearrangement is shown in continuous lines, the triplet process in dotted lines. These calculations show that rearrangements may proceed via

both the singlet and triplet forms of the rhombus C_4 . There are no lower-energy pathways that we can find to explain these rearrangements. The initial barrier of 29.5 kcal mol $^{-1}$ for the singlet process (see Fig. 8) is certainly larger than that provided to singlet C_4 by vertical Franck-Condon oxidation, which means that either some $C_4^{\cdot -}$ species have some excess energy of formation, or/and some neutral C_4 species following formation may be collisionally activated before conversion to the cation.

Is this rearrangement of C_4 unique because of the stable C_4 rhombus, or can similar rearrangements also occur for other cumulenes? We can answer this question for linear C_5 . We have made $(CC^{13}CCC)^{\cdot -}$ and charged stripped it to the neutral. The five carbons of the neutral scramble during the lifetime of the neutral in the $^{-}NR^{\cdot +}$ experiment, and we are currently examining this system theoretically to uncover the mechanism(s) of the scrambling reaction(s) (S. Dua, J.H. Bowie, unpublished and incomplete results).

This leaves several interesting questions unanswered. Why is the rhombus C_4 so stable, as it must have significant strain energy? Is it possible that it has some aromatic character [73] the explanation that has been given for the stability of neutrals like **D** (Scheme

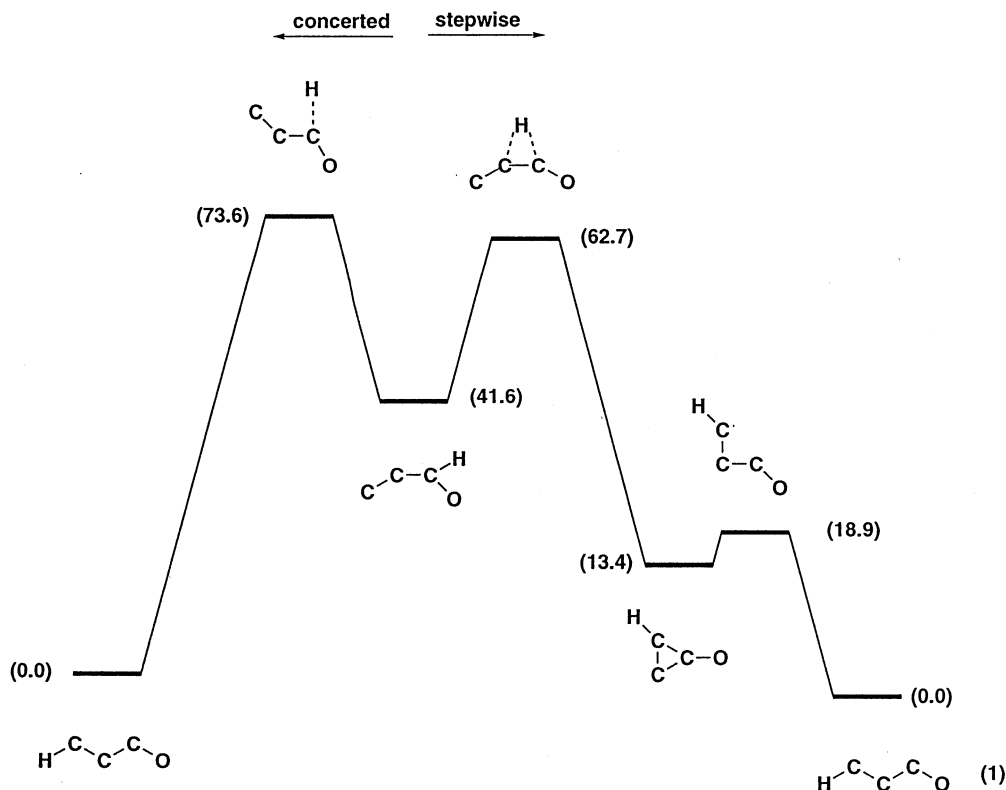
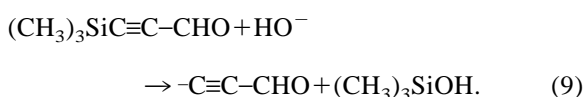
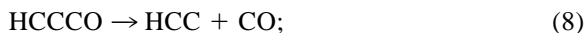


Fig. 9. Concerted and stepwise rearrangements of C_2CHO to HC_3O . Relative energies in kilocalories per mol. Energies were calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory [74].

1) [58]? Are linear and rhombus C_4 (and isomers of homologous systems [like C_5]) stellar molecules?

7. Heterocumulenes

We have examined a number of heterocumulenes containing O, S, and N. In light of the (apparent) stability of neutral C_nH and C_nH_2 , and the facile rearrangements of C_4 and C_5 , we wish to concentrate here on whether rearrangements, involving hydrogen and/or the carbon chain, occur for such systems. All experimental studies outlined below were assisted by theoretical studies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.



We have studied the isomeric radicals HCCCO and CCCHO [74]. Species HCCCO is the more stable of the two by 42 kcal mol^{-1} and does not rearrange: energized HCCCO simply fragments by the process shown in Eq. (8). The anion precursor for the isomer CCCHO is made by the route shown in Eq. (9). Charge stripping of $CCCHO^-$ does not yield the required CCCHO but, rather, the more stable HC-CCO. There are both stepwise and concerted routes to form HCCCO from CCCHO. The concerted reaction is the simpler process, involving 1,3 H transfer over a barrier of 32 kcal mol^{-1} and having an exothermicity of 42 kcal mol^{-1} . The two processes are shown in Fig. 9.

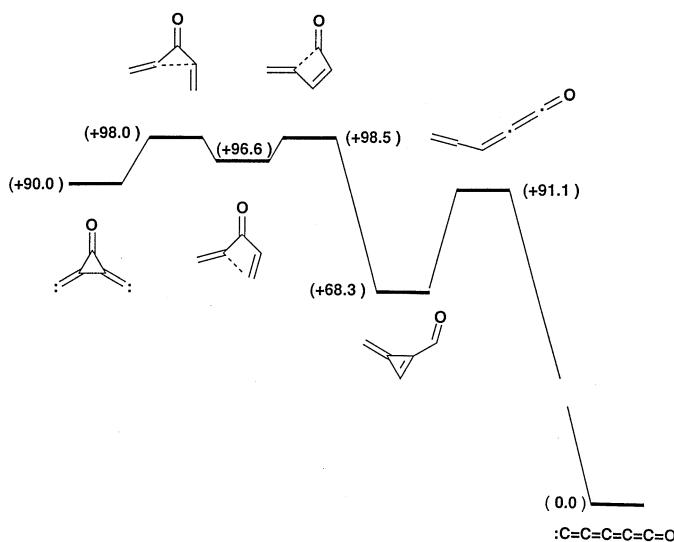
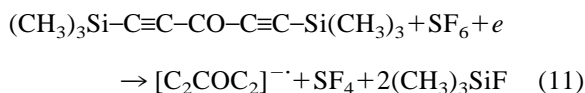
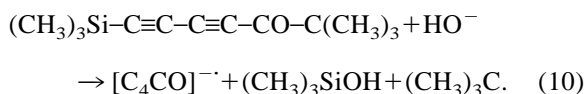
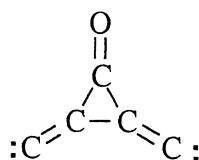


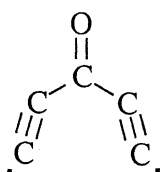
Fig. 10. The conversion of singlet C_2COC_2 to singlet C_4CO . Relative energies are in kilocalories per mol. Energies were calculated at the RCCSD(T)/aug-cc-pVDZ//B3LYP/6-31(d) level of theory. Bond connectivities and geometries (not bond orders) given for all species shown [78].



The next example, the C_5O system, is of particular interest because preliminary experiments suggest that $CCCCCO$ is present in the dark molecular cloud TMC-1 [75], together with CCO and $CCCO$ [76,77]. We have attempted to make the two neutrals $CCCCCO$ and $CCC(O)CC$ from the two anionic precursors, which were prepared as shown in Eq. (10) and (11). Charge stripping of both anions gives only $CCCCCO$. The labeled radical anion $(CC^{13}COCC)^-$



L (0 kcal mol⁻¹)



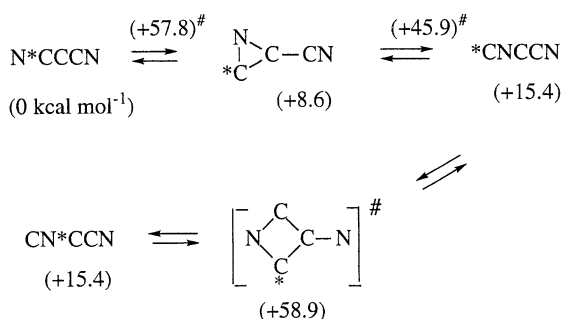
M (+20)

affords neutral $CCCC^{13}CO$ on charge stripping, as evidenced by exclusive loss of ^{13}CO in the $^-NR^+$ spectrum [78].

Theoretical data for these isomers are as follows. There are two forms of $CCCCO$, a singlet and triplet, both of which are linear. The singlet is the ground state, 56.6 kcal mol⁻¹ more negative in energy than the triplet. There are also singlet and triplet forms of C_2COC_2 ; their structures are best represented by the approximate valence bond forms **L** and **M**. Singlet **L** requires only 8 kcal mol⁻¹ of excess energy to effect rearrangement to singlet $CCCCCO$ by the sequential pathway shown in Fig. 10. Triplet **M** rearranges in concerted fashion to triplet $CCCCCO$ over a barrier of 31 kcal mol⁻¹ in a reaction exothermic by 65 kcal mol⁻¹.

Finally, consider the two neutrals $NCCCN$ and $NCCCO$. Comparison of the $^-NR^+$ and $^-CR^+$ spectra of the respective precursor anions show that the former undergoes randomization of the three carbons [79]; the latter does not [59]. Neutral $NCCCO$ is stable and, when energized, prefers to decompose to NCC and CO rather than rearrange to another isomer. The labeled negative ion precursor for $N^{13}CCCN$ is

synthesized in the source of the mass spectrometer as follows: $\text{N}^{13}\text{CCH}_2\text{CN} + \text{O}^- \rightarrow (\text{N}^{13}\text{CCCN})^- + \text{H}_2\text{O}$ [80,81]. The NR^+ and CR^+ spectra of $(\text{N}^{13}\text{CCCN})^-$ both show loss of ^{13}C and ^{12}C , but the extent of the scrambling is more pronounced in the NR^+ spectrum. Potential surface calculations suggest that the C scrambling within neutral NCCCN occurs by a nitrile to isonitrile rearrangement followed a cyclization/ring-opening mechanism. This is summarized in Scheme 3, where energies are given in kilocalories per mol. Only bond connectivities are shown for reactant, intermediates, and product. The energy required to effect this complex process is significantly higher than any excess energy provided by the vertical Franck-Condon process, with the barrier of the first step of the nitrile/isonitrile rearrangement being $57.8 \text{ kcal mol}^{-1}$. This is the largest barrier to a transition state for any of the rearrangements we have described in this article: pointing again to either excess energy of the precursor anion and/or collisional activation of the initially formed neutral in the collision cell.



Scheme 3. (* = ^{13}C , # indicates transition state, or barrier to transition state)

Having considered all the rearrangements outlined above, particularly the atom scrambling in C_4 [58] and C_5 (Dua and Bowie, unpublished data) and the H rearrangement of CCCHO to yield HCCCO [74], it seems extraordinary that the isomers that we studied in systems C_5H [65] and C_5H_2 [68] showed no evidence of significant rearrangement. There is absolutely no doubt that the NR^+ spectra of all of the various isomers are reproducibly different. Even so,

we intend to return to the first of these systems and investigate the NR^+ spectra of the doubly labeled anions $(\text{CCCC}^{13}\text{CD})^-$ and $(\text{CC}^{13}\text{CDCC})^-$. Such a project will be very challenging synthetically, but if we can make these anions, the dilemma hopefully can be resolved.

8. Conclusions and acknowledgements

It has now been 30 years since I first read the work of Beynon and Cooks on charge exchange: it was their results that catalyzed both my work and that of others on charge reversal of negative ions and on neutralization/reionization. I have had much enjoyment and satisfaction working in these areas, areas that have been the training ground for many graduate students from this laboratory. I thank them and the postdoctoral fellows and all of my collaborating colleagues for the work described in this article. I also thank the Australian Research Council for continuing financial support of all of our ion-chemistry studies.

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