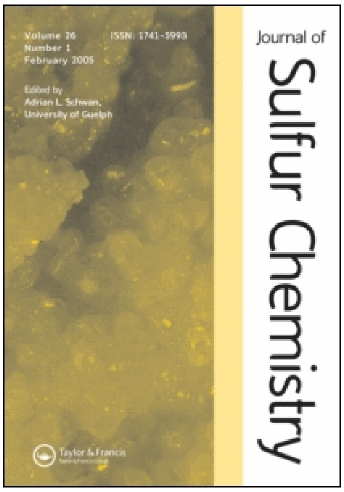

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Robert Flammang[a]; Curt Wentrup[b]
[a] Laboratory of Organic Chemistry, University of Mons-Hainaut, Mons, Belgium [b] Department of Chemistry, The University of Queensland, Brisbane, Australia

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MASS SPECTROMETRY OF $S{=}C{=}(C)_n{=}C{=}X$ CUMULENES

ROBERT FLAMMANG[a,*] and CURT WENTRUP[b]

[a]*Laboratory of Organic Chemistry, University of Mons-Hainaut, Avenue Maistriau 19, B-7000 Mons, Belgium;* [b]*Department of Chemistry, The University of Queensland, Brisbane, Qld 4072, Australia*

(Received 6 October 1998)

This review describes the applications of tandem mass spectrometry methodologies for the preparation and identification of ionized and neutral heterocumulenes $S{=}C{=}(C)_n{=}C{=}X$ in the gas phase.

Keywords: Heterocumulenes; collisional activation; neutralization–reionization; flash-vacuum pyrolysis; ion–molecule reactions

CONTENTS

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* Corresponding author.

1. INTRODUCTION

A major advance in structural organic mass spectrometry has been the introduction of collisional activation, developed mainly by the group of McLafferty.[1] In these experiments, a beam of mass-selected fast ions collides with a collision gas and, given the deposition of a large amount of energy in the ions, numerous fragmentations are observed. All these collision-induced fragments form the collision activation (CA) spectrum of the selected ions, and structural features are usually easily recognized in such a spectrum.[2]

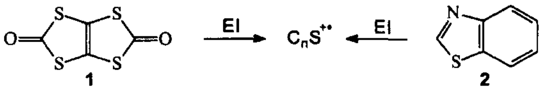
A second major advance, due again to McLafferty, has been the introduction of neutralization–reionization mass spectrometry (NRMS) consisting of sequential neutralization of fast ions into fast neutrals and reionization/fragmentation of these neutrals.[3] NR mass spectra therefore characterize the structure of the neutral molecules formed during the flight and, given the fact that the neutrals are isolated in the mass spectrometer gas phase, NRMS has allowed the production and identification of numerous reactive neutral molecules (transient molecules, hypervalent species, interstellar or atmospheric species, etc.).[4]

Flash-vacuum pyrolysis (FVP) has also been used to generate reactive molecules in the gas phase.[5] On-line coupling of FVP with mass spectrometry (FVP/MS) is technically quite simple, and, if the pyrolysis gives rise to a complex mixture, application of tandem mass spectrometry methodologies (FVP/MS/MS) often identifies the individual constituents of the pyrolyzate.[6]

These mass spectrometric methodologies have allowed the characterization of ionized or neutral cumulenic compounds of general formula $S{=}C{=}(C)_n{=}C{=}X$.

2. POLYCARBON SULFIDES, $S{=}C{=}(C)_n$

Electron impact ionization of 1,3,4,6-tetrathiapentalene-2,5-dione **1** affords as most important fragments $C_2S_n^{+\bullet}$ ($n = 1$–4) ions including the interesting $C_2S^{+\bullet}$ species.[7] The CA spectrum of these m/z 56 ions which contains the structure-indicative fragments of $CS^{+\bullet}$, $S^{+\bullet}$, $C_2^{+\bullet}$ and $C^{+\bullet}$ is only compatible with the CCS connectivity. If $C_2S^{+\bullet}$ ions are subjected to an NRMS experiment, one obtains not only a very abundant recovery signal at *m/z* 56, but also a fragmentation pattern virtually identical with the CA spectrum. It is thus concluded that a stable

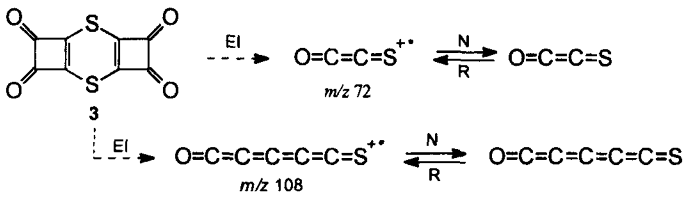


C=C=S species, was formed. The same species has been found in the electron ionization mass spectrometry (EIMS) of benzothiazole **2**.[8] Albeit in very low abundance (less than 1%), the CA and NR spectra are indeed similar to those reported previously.[7] In fact, benzothiazole **2** molecular ions are found to generate a whole series of polycarbon monosulfide ions, $C_nS^{+\bullet}$ ($n = 2$–6). The NR mass spectra of these ions are characterized in all cases by a significant recovery signal, thus pointing to the stability of the vinylidenes in the gas phase.

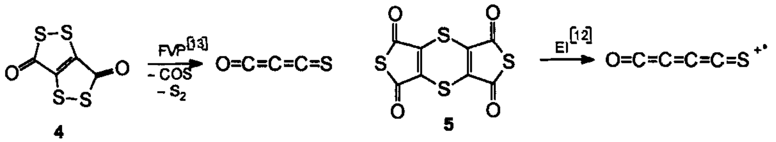
The C_nS species are of considerable astrophysical interest. The free radical C_2S has been identified in both TMC1 and Sgr B2.[9] Its ionization energy and proton affinity have been established theoretically.[10]

3. POLYCARBON OXYSULFIDES, $S{=}C{=}(C)_n{=}C{=}O$

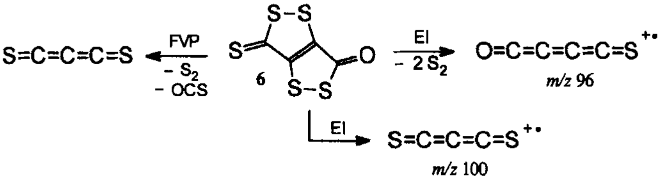
The elusive thioxoethenone, O=C=C=S, can readily be generated by reduction of the corresponding radical cation in an NRMS experiment. The precursor of the radical cations is again a heterocyclic molecule **3**.[11]



The higher homologue, OCCCS, and its radical cation or radical anion have also been characterized using CA and NR spectra,[12,13] starting again with appropriate heterocyclic precursors, **3** and **4**. Similar experimental evidence is reported for the existence of the higher homologues OCCCCS (from **5**) and OCCCCCS (from **3**).[12]

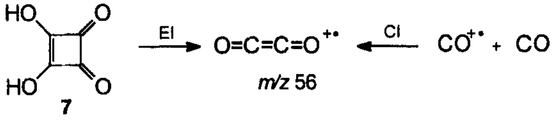


OCCCCS radical cations have been produced by dissociative ionization of 1,2-dithiolo[4,3-*c*]dithiol-3-one-6-thione **6**.[13] Although a similar behaviour of heterocyclic compounds upon ionization or FVP is frequently noted, in the present case **6** prefers to dissociate thermally into SCCCS, S_2 and COS. It is suggested that this is the result of a lower relative stability of OCCCCS in the neutral state than in the ion. Neutral cumulenes possessing an even number of carbon atoms are indeed less stable than cumulenes with an odd number of carbons.[14]



4. POLYCARBON DISULFIDES, S=C=(C)$_n$=C=S

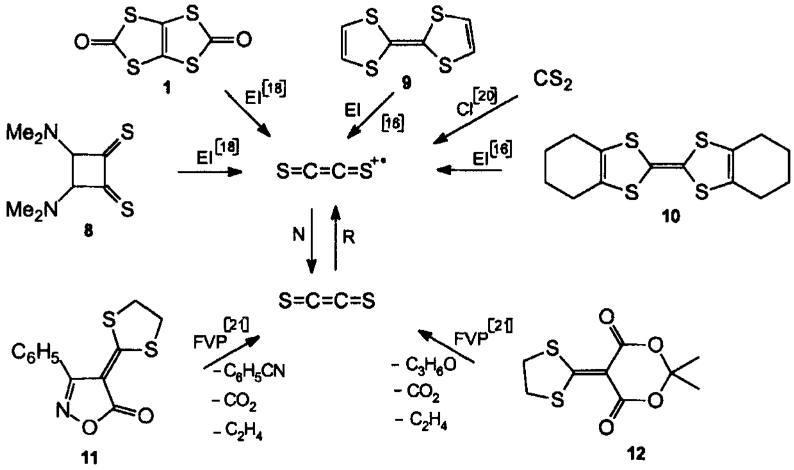
Despite extensive efforts, ethenedione, OCCO, is still an unknown molecule although the corresponding radical cation has been convincingly characterized by collisional activation mass spectrometry from quite different sources.[15,16] The ions have been prepared by dissociative ionization of squaric acid **7** or by clustering $CO^{+\bullet}$ with CO under chemical ionization conditions.



The observation of a recovery signal in an NR spectrum has been described,[17] but the possibility that it is due to background ions has not been excluded.[18]

In contrast, ethenedithione, SCCS, is very easily generated as radical cations by dissociative ionization of various precursors **1**, **8**–**10**.[16,19] The stability of the corresponding neutrals is unambiguously confirmed by NR and NR/CA (collisional activation of the ions forming the recovery signal) experiments. Chemical ionization of carbon disulfide at relatively high pressure (*ca.* 1 Torr) is also another convenient source of SCCS radical cations although the major ion–molecule product is the CS_3 radical cation.[20]

Since NRMS experiments predict neutral ethenedithione, S=C=C=S, to be stable in the gas phase, heterocyclic precursors were sought for its preparation using FVP. Indeed, by using a combination of FVP/MS/MS and matrix IR, it has been shown that Meldrum's acid **12** and the isoxazolone **11** are excellent precursors of ethenedithione in the gas phase. In the former case, an intermediate propadienone has been detected at moderate FVP temperatures.[21]



The modification of the mass spectrum of the isoxazolone **11** as a function of temperature is illustrated in Figure 1. Pyrolysis products are clearly indicated at *m*/*z* 159, 103/76, 88, and 44 ascribed to $[C_6H_5,C_3,N,S]$, benzonitrile, SCCS and CO_2, respectively.

Heterocumulenes having an odd number of carbons are more stable than their analogues with an even number of carbons.[14] Thus, carbon subsulfide, SCCCS, is stable enough to allow isolation for a short time at room temperature. It is therefore not surprising that the NR spectrum

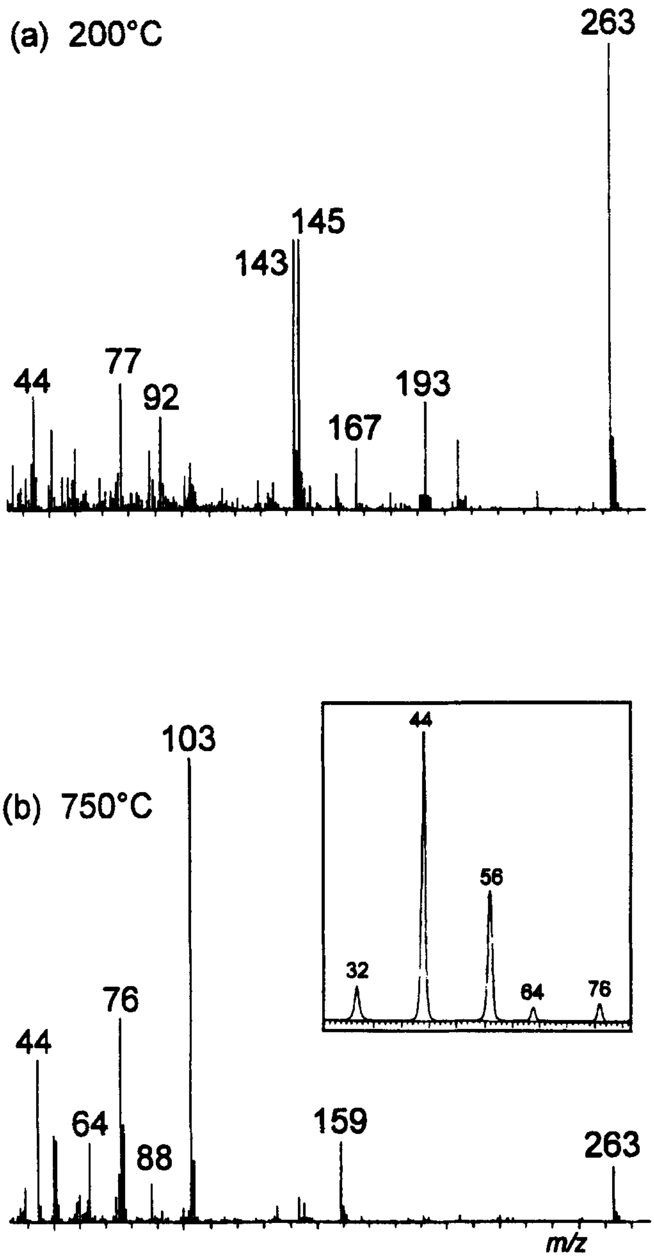
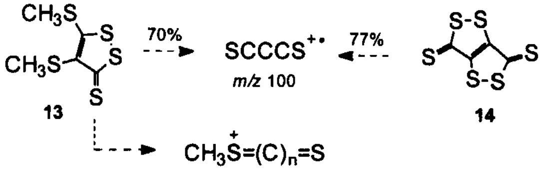
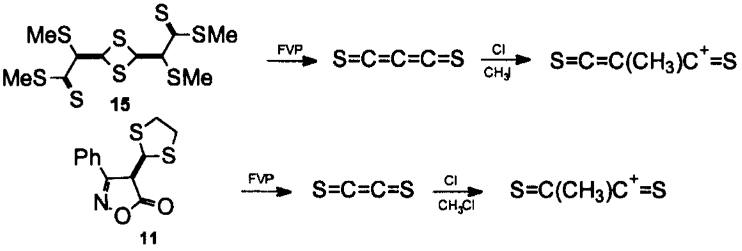


FIGURE 1 Electron ionization mass spectra of the isoxazolone **11** at two different oven temperatures; the inset shows the CA spectrum of the m/z 88 ions.

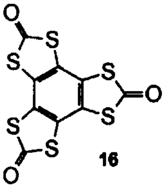
of the corresponding radical cations features a very intense recovery signal.[22,13] The SCCCS$^{+\bullet}$ ions have been produced in high yields by dissociative electron ionization of the dithiolethiones **13** and **14**.



In fact, the bis(methylthio)dithiolethione **13** has allowed the detection of a series of carbon disulfide radical cation, $SC_nS^{+\bullet}$ ($n = 1-3$) and their *S*-methylated forms, $CH_3SC_nS^+$, in the gas phase.[22] The thermodynamically more stable *C*-methylated SCCS and SCCCS were produced using a combination of FVP of the dithietane **15** and the isoxazolone **11** and chemical ionization with alkyl halides as the reagent gas.



Another efficient entry for the generation of a whole series of $C_nS_2^{+\bullet}$ ($n = 2-6$) ions has been found with compound **16**.[23] The connectivities of these cumulenes are clearly reflected in their CA spectra. Typical fragments, for example for $C_4S_2^{+\bullet}$, are indeed observed at *m*/*z* 68 (CCCS$^{+\bullet}$), 56 (CCS$^{+\bullet}$) and 36 (CCC$^{+\bullet}$). The observation of the same reactions in the NR mass spectrum (Figure 2) and the presence of an intense recovery signal corresponding to "survivor" ions indicate that the neutral cumulene is perfectly stable when isolated in the gas phase.



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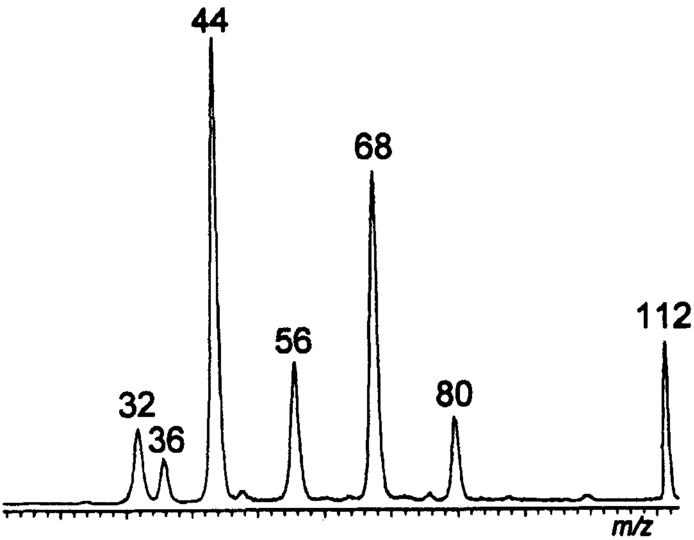
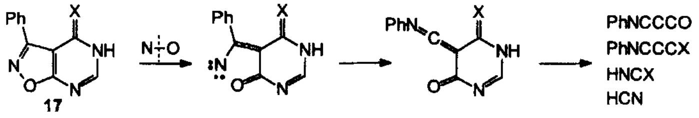


FIGURE 2 NR (xenon/oxygen) mass spectrum of $C_4S_2^{+\bullet}$ radical cations.

5. IMINOPROPADIENETHIONES (RN=C=C=C=S) AND IMINOETHENETHIONES (RN=C=C=S)

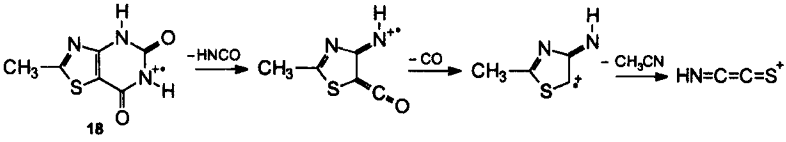
The identification of monoimines derived from carbon suboxide, RNCCCO, was reported only recently by using a combination of techniques: NRMS, FVP/MS, FVP/IR and trapping experiments.[24] The first precursor used was the phenylisoxazolopyrimidinone **17** (X = O) which shows the same behaviour upon electron ionization and FVP. The first step consists of the cleavage of the labile N–O bond of the isoxazole ring producing a putative vinylnitrene. Rearrangement of the nitrene into a ketenimine follows readily and the so-produced diazacyclohexenedione undergoes a retro Diels–Alder reaction into PhNCCCO (as ions in electron ionization, or neutrals in FVP) plus HCN + HNCO.



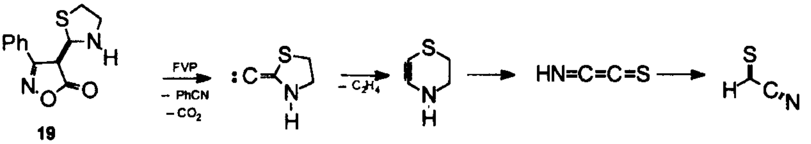
A similar approach has been used in the identification of phenyliminopropadienethione, PhNCCCS.[25] Upon electron ionization,

17 (X = S) generates intensively *m*/*z* 159 ions (base peak of the mass spectrum) presenting the expected propadiene connectivity. The NR mass spectrum of these ions features an intense recovery signal but differs from the corresponding CA spectrum by new peaks at *m*/*z* 82, 68, 56 and 44 ascribed to reionization of SCCCN$^\bullet$ radicals lost in the neutralization cell. Although the stability of neutral PhNCCCS is proved in the NR experiment, FVP/MS indicate that **17** (X = S) produces mainly PhNCCCO, not PhNCCCS. A small amount of this last cumulene has been detected in an FVP/IR experiment (18 K, argon matrix).

Iminoethenethione, HNCCS, is also a stable molecule on the microsecond time scale of the NRMS experiment.[26] The corresponding radical cations have been generated starting with the molecular ions of thiazolopyrimidinedione **18**, which undergo in sequence the following fragmentations: retro Diels–Alder reaction of the pyrimidine ring, decarbonylation of the intermediate α-iminoketene ions, and ring fragmentation of the so-produced α-iminocarbene.



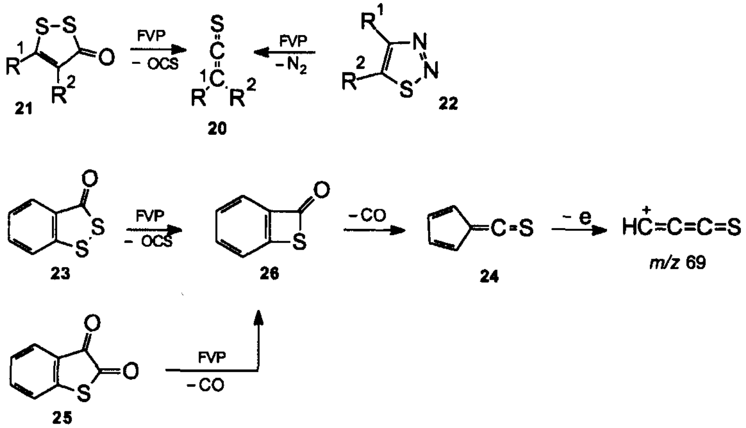
Since the thiazolopyrimidinedione **18** is completely stable under FVP conditions, another heterocyclic precursor was prepared. The isoxazolone **19** fragments thermally in a manner similar to that of **11** above, to produce benzonitrile, carbon dioxide and ethene in a reaction sequence involving a putative vinylidene intermediate and its product of ring expansion, a cyclohexyne. Retro Diels–Alder reaction of this strained intermediate completes the sequence. In fact, the CA spectrum of the C_2HNS product presents a very strong signal at *m*/*z* 45 (H–C$^+$=S ions) indicating that HN=C=C=S easily tautomerizes to thioformyl cyanide, H–C(=S)CN, via wall collisions. These MS results were supported by matrix IR experiments.[26]



6. THIOKETENES ($R_2C{=}C{=}S$)

Mass spectrometry evidence for the generation of thioketene (**21**, $R^1 = R^2 = H$) in the gas phase has been provided in the pyrolysis of labelled methyl dithioacetate, $CH_3C(^{34}S)SCH_3$, presumably via the enethiol intermediate $CH_2{=}C(^{34}SH)SCH_3$.[27]

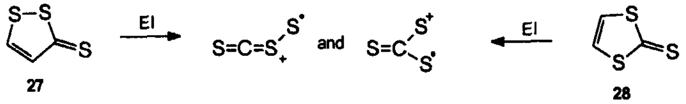
More recently, it has been established that thioketenes **21** are formed in a Wolff-type rearrangement, together with OCS, on FVP of 1,2-dithiole-3-ones **20** as well as 1,2,3-thiadiazoles **22**. The thioketenes were identified by a combination of argon matrix isolation FTIR spectroscopy and collisional activation mass spectrometry.[28,29] These techniques also allowed the characterization of the cyclopentadienoid thioketene **24**, using either benzo-1,2-dithiol-3-one **23** or benzothiophenedione **25** as the precursors. In the latter case, the reaction proceeds via the observable thietone **26**.[28] The base peak of the CA spectrum of the molecular ion of thioketene **24** corresponds to protonated tricarbon sulfide ions, $S{=}C{=}C{=}C^+{-}H$.



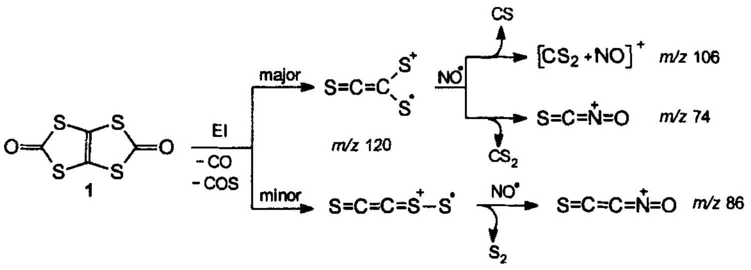
7. VARIOUS

Very recently, experimental and theoretical data for the characterization of a series of ionized (poly)carbon disulfide *S*- (or *C*-) sulfides of the general formulas $S(C_n)S^+S^\bullet$ and $S(C_n)(S^+)S^\bullet$ have been published.

Dissociative ionization (loss of ethyne) of the dithiolethiones **27** and **28** is a convenient source of $CS_3^{+\bullet}$ radical cations. On the basis of the structure of the precursors, isomeric species are expected, but the CA and NR spectra of these *m/z* 108 ions feature identical fragmentations, thus suggesting the occurrence of a mixture of isomers.[20] This has been proved by using labelled dithiolethiones.[30] The distonic $SCS^+S^\bullet$ species was predicted to be a global minimum on the potential energy surface while the $SC(S^+)S^\bullet$ is predicted to be less stable by 42 kJ mol^{-1}.[20]



The $C_2S_3^{+\bullet}$ ions (*m/z* 120), higher homologues of the CS_3 radical cations, have been produced by dissociative ionization of the isomeric dithiolodithioolediones **1** and **4** by consecutive loss of CO and COS. Again, CA (high and low translational energies of the ions) and NR mass spectrometries appear to give ambiguous information on their connectivities.[31] In contrast, ion–molecule reactions with nitric oxide readily differentiate between the $SCCS_2^{+\bullet}$ and $SCCSS^{+\bullet}$ species. This is illustrated in the following scheme for the $C_2S_3^{+\bullet}$ ions of dithiolodithioledione **1**; the relative abundances of the ion–molecule products *m/z* 106/74 and *m/z* 86 are reversed in the case of **4** (Figure 3). The mass and collisional activation spectra of these ion–molecule reaction products have been recorded on a new type of hybrid mass spectrometer featuring an (EBE) sectors–quadrupole-(EBE) sectors configuration.[32]



The reaction between the $SCCSS^{+\bullet}$ ions and methyl isocyanide proceeds with elimination of disulfur; iminopropadienethione ions, $CH_3N{=}C{=}C{=}C{=}S^{+\bullet}$, are produced in this experiment as evidenced by

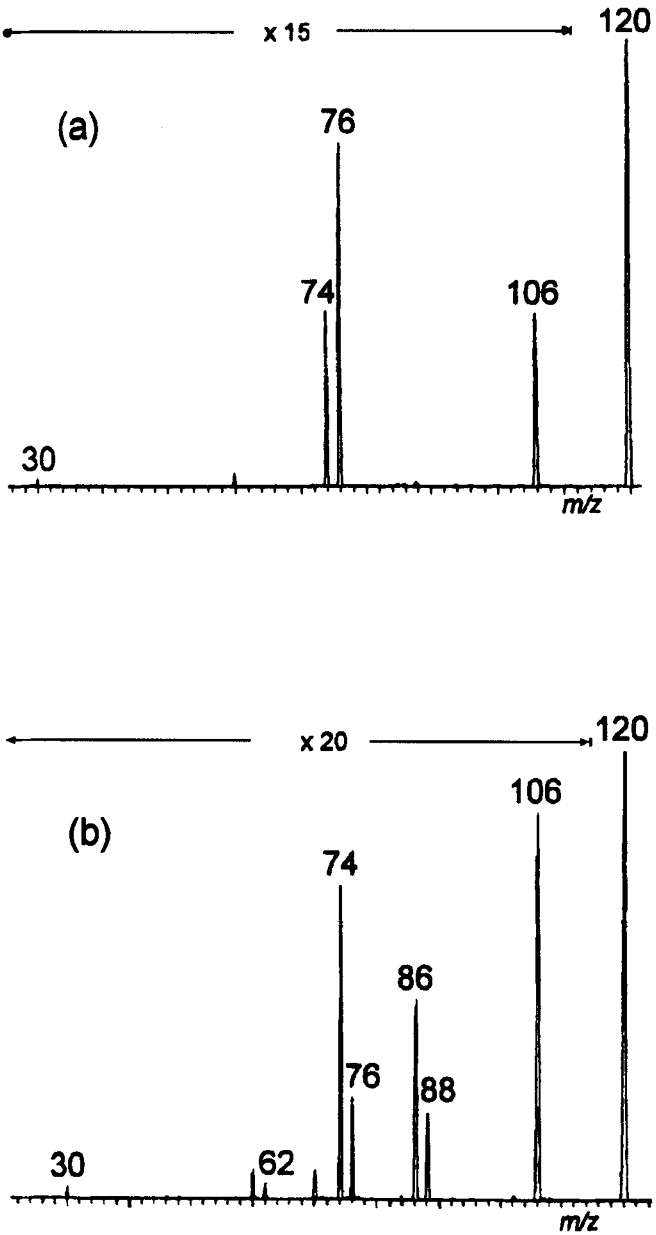


FIGURE 3 Ion–molecule reactions between mass-selected *m/z* 120 ions with nitric oxide in an r.f.-only quadrupole collision cell: the *m/z* 120 ions were generated by dissociative ionization of **1** (a) and **4** (b).

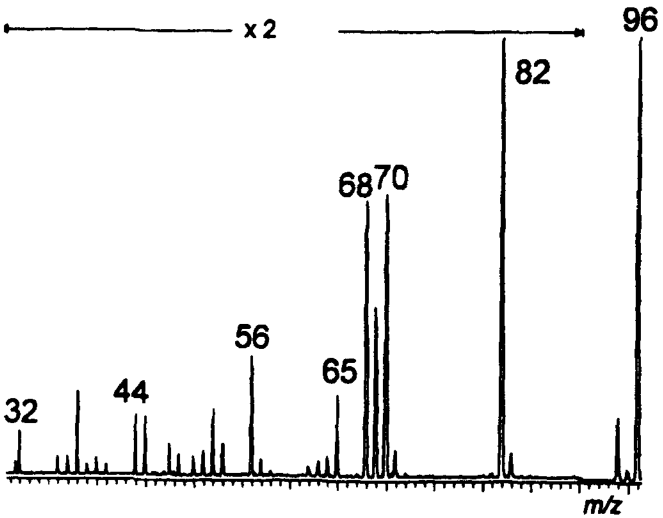
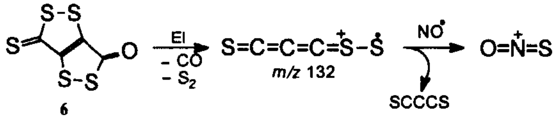


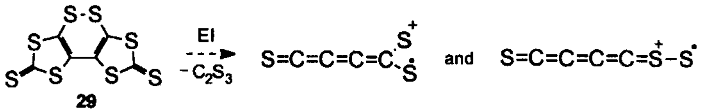
FIGURE 4 CA mass spectrum of *m/z* 97 ions, $[CH_3N{=}C{=}C{=}C{=}S]^{+\bullet}$, produced in the ion–molecule reaction of $C_2S_3^{+\bullet}$ ions generated from **4** and methyl isocyanide.

the high energy CA spectrum depicted in Figure 4 (characteristic peaks at *m/z* 82, 68, 65 and 56).

Decarbonylation is the lowest energy decomposition pathway of the metastable molecular ions $\mathbf{6}^{+\bullet}$, and the resulting ions are responsible for the consecutive production of $C_3S_3^{+\bullet}$ ions (loss of S_2). Their SCCCSS connectivity has been proposed on the basis of the reactivity towards nitric oxide generating exclusively SNO^+ cations.[13]



$C_4S_3^{+\bullet}$ radical cations have been found in the electron ionization mass spectrum of compound **29**.[33] As expected on the basis of the cumulogy principle,[34] their behaviour upon ion–molecule reaction with nitric oxide is similar to what has been observed for the $C_2S_3^{+\bullet}$ species.



8. CONCLUSIONS

The development of recent mass spectrometric methodologies has extended the capabilities of the mass spectrometer to the study not only of ionized species, but also neutral molecules inaccessible under conventional reaction conditions. The predictive power of NRMS can also be used as a valuable complement to other techniques such as FVP/matrix isolation. Moreover, insertion of a quadrupole collision cell between the electric and magnetic sectors of a tandem mass spectrometer makes it possible to perform associative ion–molecule reactions and high energy collisional activation of the products. The importance of heterocyclic precursor molecules in many of the examples presented here is stressed.

REFERENCES

[1] (a) F.W. McLafferty, R. Kornfeld, F.W. Haddon, K. Levsen, I. Sakai, P.F. Bente III, S.-C. Tsai and H.D.R. Schuddemage, *J. Amer. Chem. Soc.*, **95**, 1695 (1973); (b) F.W. McLafferty, P.F. Bente III, R. Kornfeld, S.-C. Tsai and I. Howe, *J. Amer. Chem. Soc.*, **95**, 2120 (1973).

[2] For recent reviews, see: (a) S.A. McLuckey, *J. Am. Soc. Mass Spectrom.*, **3**, 599 (1992); (b) R.G. Cooks, *J. Mass Spectrom.*, **30**, 1215 (1995).

[3] F.W. McLafferty, P.J. Todd, D.C. McGilvery and M.A. Baldwin, *J. Amer. Chem. Soc.*, **102**, 3360 (1980).

[4] For recent reviews, see: (a) N. Goldberg and H. Schwarz, *Acc. Chem. Res.*, **27**, 347 (1994); (b) R. Flammang and C. Wentrup, *Sulfur Reports*, **20**, 255 (1997); (c) C.A. Hornung, G. Hornung, D. Schröder and H. Schwarz, *Chem. Soc. Rev.*, **27**, 91 (1998).

[5] (a) R.F.C. Brown, *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York, 1980; (b) Y. Vallée, *Gas Phase Reactions in Organic Synthesis*, Harwood Academic Publishers, 1997.

[6] J. Brown, R. Flammang, Y. Govaert, M. Plisnier, C. Wentrup and Y. Van Haverbeke, *Rapid Commun. Mass Spectrom.*, **6**, 249 (1992).

[7] D. Sülzle and H. Schwarz, *Chem. Ber.*, **122**, 1803–1805 (1989).

[8] R. Flammang, Y. Van Haverbeke, M.W. Wong and C. Wentrup, *Rapid Commun. Mass Spectrom.*, **9**, 203–208 (1995).

[9] S. Saito, K. Kawaguchi, S. Yamamoto, M. Ohishi, F. Suzuki and N. Kaifu, *Astrophys.*, **317**, L115 (1987).

[10] R.G.A.R. Mclagan and P. Sudkeaw, *Chem. Phys. Lett.*, **194**, 147 (1992).

[11] D. Sülzle, J.K. Terlouw and H. Schwarz, *J. Am. Chem. Soc.*, **112**, 628 (1990).

[12] D. Sülzle and H. Schwarz, *J. Am. Chem. Soc.*, **113**, 48 (1991).

[13] C. Th. Pedersen, R. Flammang, P. Gerbaux and E. Fanghänel, *J. Chem. Soc. Perkin Trans. 2*, 1403 (1998).

[14] D. Sülzle and H. Schwarz, in *Fundamentals of Gas Phase Ion Chemistry*, K.R. Jennings (Ed.), Kluwer Academic Publishers, Netherlands, 1991.

[15] D. Sülzle, T. Weiske and H. Schwarz, *Int. J. Mass Spectrom. Ion Processes*, **125**, 75–79 (1993).

[16] M. Plisnier, Ph.D. Thesis, University of Mons-Hainaut, 1992.
[17] H. Chen and J.L. Holmes, *Int. J. Mass Spectrom. Ion Processes*, **133**, 111 (1994).
[18] D. Schröder and H. Schwarz, *Int. J. Mass Spectrom. Ion Processes*, **147**, 183–193 (1995).
[19] D. Sülzle and H. Schwarz, *Angew. Chem. Int. Ed. Engl.*, **27**, 1337 (1988).
[20] P. Gerbaux, Y. Van Haverbeke, R. Flammang, M.W. Wong and C. Wentrup, *J. Phys. Chem. A*, **101**, 6970 (1997).
[21] C. Wentrup, P. Kambouris, R.A. Evans, D. Owen, G. Macfarlane, J. Chuche, J.C. Ben Cheikh, A. Ben Cheikh, M. Plisnier and R. Flammang, *J. Am. Chem. Soc.*, **113**, 3130–3135 (1991).
[22] M.W. Wong, C. Wentrup and R. Flammang, *J. Phys. Chem.*, **99**, 16849 (1995).
[23] D. Sülzle, N. Beye, E. Fanghänel and H. Schwarz, *Chem. Ber.*, **123**, 2069 (1990).
[24] (a) T. Mosandl, C.O. Kappe, R. Flammang and C. Wentrup, *J. Chem. Soc. Chem. Commun.*, 1571 (1992); (b) R. Flammang, S. Laurent, M. Flammang-Barbieux and C. Wentrup, *Rapid Commun. Mass Spectrom.*, **6**, 667 (1992).
[25] R. Flammang and C. Wentrup, unpublished results.
[26] R. Flammang, D. Landu, S. Laurent, M. Barbieux-Flammang, C.O. Kappe, M.W. Wong and C. Wentrup, *J. Amer Chem. Soc.*, **116**, 2005 (1994).
[27] L. Carlsen and H. Egsgaard, *J. Chem. Res.* (*S*), 340 (1984).
[28] T. Jørgensen, C.Th. Pedersen, R. Flammang and C. Wentrup, *J. Chem. Soc., Perkin Trans. 2*, 173 (1997).
[29] For earlier work, see G. Seybold and C. Heibl, *Angew. Chem., Int. Ed. Engl.*, **14**, 248 (1975); G. Seybold and C. Heibl, *Chem. Ber.* **110**, 1225 (1977); E. Schaumann, *Tetrahedron* **44**, 1827 (1988); E. Schaumann in *Houben-Weyl, Methoden der Organischen Chemie*, D. Klamann, Ed., Thieme, Stuttgart, 1985, Vol. E11/1, p. 232.
[30] D. Sülzle, H. Egsgaard, L. Carlsen and H. Schwarz, *J. Am. Chem. Soc.*, **112**, 3750 (1990).
[31] P. Gerbaux, R. Flammang, C.Th. Pedersen and M.W. Wong, *J. Phys. Chem. A*, submitted for publication.
[32] R. Flammang, Y. Van Haverbeke, C. Braybrook and J. Brown, *Rapid Commun. Mass Spectrom.*, **9**, 795 (1995).
[33] R. Flammang, P. Gerbaux and C.Th. Pedersen, in preparation.
[34] M. Parmentier, J. Galloy, M. Van Meersche and H.G. Viehe, *Angew. Chem. Int. Ed. Engl.*, **14**, 53 (1975).