3,6-Dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3,6-dithione and oxo analogues: a comparative study of the thermal (FVP) and electron ionization (EI) induced fragmentations

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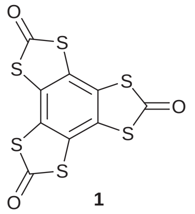
Flash-vacuum pyrolysis (FVP) of the dithiolodithioledithione 2 in the 700–1000 °C temperature range affords carbon subsulfide, carbon disulfide and disulfur with high yields. This has been demonstrated by using a combination of FVP/IR (argon matrix) and FVP/MS(MS) experiments. S=C=C=C=C=S is generated as ions by dissociative ionization of 2, not as neutrals upon pyrolysis. Similar behaviour is noted for the oxygen analogue 4: pyrolytic formation of carbon subsulfide, carbon oxysulfide and disulfur. It is also demonstrated that, upon dissociative ionization, dithiolodithioledione 3 and thioxodithiolodithiolone 4 constitute an interesting source of new cumulenic ions derived from carbon subsulfide and carbon oxysulfide, tentatively assigned as $SCCCS^+$–$S^\bullet$ and $OCCCS^+$–$S^\bullet$ radical cations by collisional activation (high and low energy) experiments and ion–molecule reactions with nitric oxide.

Introduction

Heterocumulenes of general structure S=C(C)$_n$C=S ($n = 0$–4) have attracted exceptional interest in recent years as some of them have been observed by astrophysicists in interstellar space and have been postulated as key intermediates in the formation of interstellar species.[1,2] As a result of their high intermolecular reactivity, most of these molecules cannot be isolated under 'ordinary' conditions, especially when they contain an even number of carbon atoms. In order to gain more insight into the thermal formation of such compounds from 1,2-dithiole compounds we have investigated the thermolysis of a series of 1,2-dithiole derivatives.[3–7]

In the gas phase, a whole series of S=C(C)$_n$C=S cumulenes ($n = 0$–4) has been prepared[8] by reduction of the corresponding radical cations starting with a single precursor **1**. Identification of the connectivity was performed by reionization of the neutral molecules in the so-called neutralization–reionization experiment (NRMS).[9] For example, S=C=C=C=C=S was unambiguously identified by intense peaks at *m*/*z* 68 ($CCCS^{\bullet+}$), 56 ($CCS^{\bullet+}$), 36 ($CCC^{\bullet+}$) and also by an intense recovery signal corresponding to 'survivor' ions.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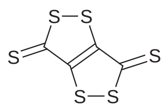
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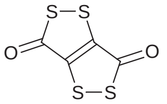
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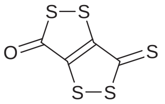
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Additionally another efficient precursor of $C_4S_2^{\bullet+}$ ions was found with the dithiolodithiole **2**, which also gave rise to an intense signal at *m*/*z* 112 after electron ionization (EI). The fact that these ions present the SCCCCS connectivity was also established by collisional activation (CA) and NR spectra identical to those recorded for the precursor **1**.[10]

The predictive aspect of NRMS concerning the gas phase stability of reactive molecules is an invaluable help for further studies which have more preparative potential, like flash-vacuum pyrolysis (FVP).[11] Moreover, a common behaviour of heterocyclic precursors upon electron ionization and FVP has been frequently reported in the literature.[12] We therefore decided to investigate in more detail the fragmentation induced by electron ionization of **2** and its oxo analogues **3** and **4** as well as their thermal (FVP) fragmentation, the monitoring of the pyrolyzates being performed by matrix infrared spectroscopy and on-line tandem mass spectrometry.

During the present study, radical cations of composition C_3OS_2 and C_3S_3 have also been observed upon dissociative ionization of **3** and **4** respectively. The structure of these peculiar species has been investigated making use of the extended capabilities of a new hybrid tandem mass spectrometer.

Results and discussion

Flash-vacuum pyrolysis of 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]-dithiole-3,6-dithione (2)

The electron ionization mass spectrum (EIMS) of **2** features significant peaks at *m*/*z* 240 ($M^{\bullet+}$, 100%), 164 (loss of CS_2, 15%), 112 ($C_4S_2^{\bullet+}$, 56%), 100 ($C_3S_2^{\bullet+}$, 77%), 88 ($C_2S_2^{\bullet+}$, 25%) and 76 ($CS_2^{\bullet+}$, 19%). Low energy metastable molecular ions fragment only by losing carbon disulfide giving *m*/*z* 164 ions which, in turn, are responsible for the generation of the *m*/*z* 100 ions. The *m*/*z* 112 ions are only seen in the (high energy) CA spectrum of the molecular ions. Collisional activation of the mass-selected *m*/*z* 112 and 100 ions confirms their SCCCCS and SCCCS connectivities respectively as the CA spectra are identical to those reported in the literature.[4,8]

The dithiolodithiole **2** appeared to be very stable upon short contact time FVP and in order to induce a significant degree of fragmentation a small piece of quartz wool was introduced in the pyrolysis tube. Under these conditions, at 750 °C, the mass spectrum of **2** is modified: *m*/*z* 240 (26%), 164 (4%), 112 (20%), 100 (88%), 88 (11%), 76 (100%) and 64 (82%). The main pyrolysis products detected are therefore C_3S_2, CS_2 and S_2.

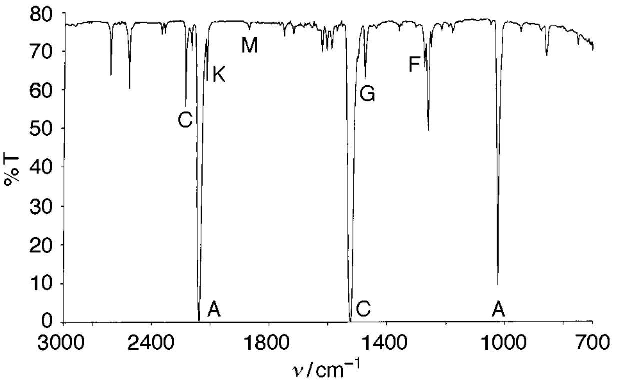
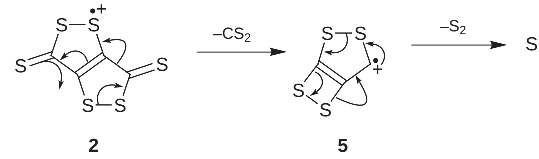


Fig. 1 IR spectrum (10 K argon matrix) of the pyrolysis products of compound **2** (1000 °C, 10^{-5} mbar). No significant peaks are present above 3000 cm^{-1}. Bands due to C_3S_2 (A) at 1024 and 2077 cm^{-1}, CS_2 (C) at 1526 and 2177 cm^{-1}, CS (F) at 1274 cm^{-1}, $^{13}CS_2$ (G) at 1477 cm^{-1}, $S^{13}CC_2S$ (K) at 2031 cm^{-1}, C_4S_2 ? (M) at 1873 cm^{-1} are labelled.

Formation of C_4S_2 is not observed. This can probably be attributed to a larger stability difference between SCCCCS and SCCCS in the neutral state than in the ionized state.

The result of an IR matrix isolation experiment on the FVP products of **2** is shown in Fig. 1. In good agreement with the MS data, strong absorptions are seen at 2077, 1024 cm^{-1} and 2177, 1526 cm^{-1} ascribed to carbon subsulfide (SCCCS) and carbon disulfide (SCS) respectively. A very small peak is detected at 1873 cm^{-1} which is in turn the position of the strongest band in the published IR spectrum of C_4S_2.[13] The fact that C_4S_2 is not directly observable in the FVP/MS experiment may be due to the direct formation of the *m*/*z* 112 ions by dissociative ionization of unpyrolyzed material **2** which may obscure a small increase in the amount of C_4S_2. It is also worth noting that the temperature conditions were higher in the IR experiment.

The results indicate a good correlation between the behaviour of **2** upon EI and FVP. The difficult access to C_4S_2 in the FVP experiment may be ascribed to the lower stability of the neutral cumulene which has an even number of carbon atoms. Concerning the mechanism for the formation of $C_3S_2^{\bullet+}$ ions, it is tentatively proposed that the molecular ions of **2** expel carbon disulfide which produces the cyclic carbene radical cations $\mathbf{5}^{\bullet+}$ (Scheme 1). It has been recently shown that heterocyclic carbenes such as 2,3-dihydrothiazol-2-ylidene are stable species in the gas phase as radical cations as well as neutrals.[14,15] Sterically hindered carbenes have also been isolated in the solid state.[16] Consecutive loss of disulfur finally yields ionized carbon subsulfide. The mechanism proposed in Scheme 1 holds also for the thermal fragmentation of **2**.



Scheme 1

Flash-vacuum pyrolysis of 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]-dithiole-3,6-dione (3)

If the mechanism shown in Scheme 1 occurs in the case of the dione **3**, one should expect consecutive losses of SCO and SO from the molecular ions (giving SCCCS radical cations, *m*/*z* 100) and also consecutive losses of two S_2 molecules (giving OCCCCO ions, *m*/*z* 80). In fact, the fragmentation of $\mathbf{3}^{\bullet+}$ is completely different and the most intense signals in the EIMS are seen at *m*/*z* 208 ($M^{\bullet+}$, 100%), 116 (loss of CO + S_2, 35%), 88 (SCCS ions, 52%), 76 (SCS ions, 22%) and 64 (S_2 ions, 24%).

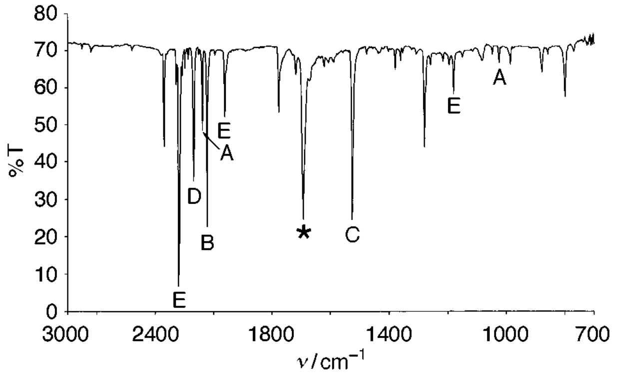
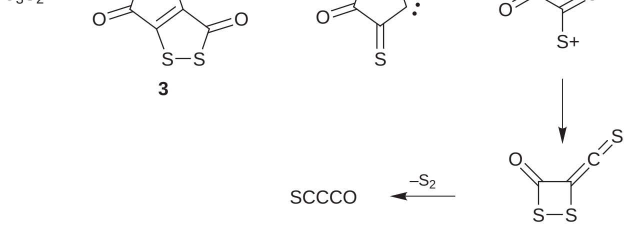


Fig. 2 IR spectrum (10 K argon matrix) of the pyrolysis products of compound **3** (1000 °C, 10^{-5} mbar). No significant peaks are present above 3000 cm^{-1}. Bands due to C_3S_2 (A) at 2078 and 1024 cm^{-1}, SCO (B) 2049 cm^{-1}, CS_2 (C) at 1527 cm^{-1}, CO (D) at 2138 cm^{-1}, SC_3O (E) at 1276 (sh), 1963 and 2243 cm^{-1} and unpyrolyzed starting material (*) are labelled.

The low energy fragmentations of the metastable molecular ions are the competitive losses of CO (*m*/*z* 180) and SCO (*m*/*z* 148). These ions are of very low intensity in the mass spectrum (*ca.* 2%). The production of the *m*/*z* 116 ions is a high energy process (only observed upon collisional activation of the molecular ions). The CA spectrum of these peculiar ions having the composition C_3OS_2 will be discussed in the last section of this paper.

Upon FVP at 750 °C, the mass spectrum is modified featuring intense peaks at *m*/*z* 208 (79%), 116 (26%) and 88 (46%) corresponding to unpyrolyzed material and *m*/*z* 100 (SCCCS ions, 27%), 84 (OCCCS, 26%), 76 (SCS ions, 83%), 64 (S_2 ions, 100%) and 60 (SCO ions, 88%) corresponding to pyrolysis products. These attributions are readily confirmed by FVP/IR (Fig. 2). OCCCCO, which is known to have a strong absorption band at 2130 cm^{-1},[17] is not observed. This is in agreement with the MS data.

The formation of OCCCS can be rationalized by the mechanism depicted in Scheme 2 involving a dithietane intermediate.



Scheme 2

However, in this case the formation of carbon subsulfide by a mechanism analogous to the one depicted in Scheme 1 is not straightforward as SO is not detected in the MS and IR experiments.

Flash-vacuum pyrolysis of 6-thioxo-3,6-dihydro[1,2]dithiolo-[4,3-*c*][1,2]dithiol-3-one (4)

The EI mass spectra of **4** are shown in Fig. 3. Without FVP, the spectrum is quite complex displaying intense peaks at *m*/*z* 224 ($M^{\bullet+}$), 196 (loss of CO), 132 (loss of CO and S_2), 120 (loss of CO and CS_2), 100 (SCCCS ions), 96 (OCCCCS ions), 88 (SCCS ions), 76 (SCS ions) and 64 (S_2 ions).

After FVP at 750 °C, the spectrum [Fig. 3(b)] is greatly simplified showing major peaks for SCCCS, SCS, S_2 and SCO respectively at *m*/*z* 100, 76, 64 and 60. IR spectroscopy is again in close agreement with the MS data, principal absorptions being indeed observed at 2078, 1024 cm^{-1} (SCCCS), 2049 cm^{-1} (SCO) and 1527 cm^{-1} (SCS) (Fig. 4). OCCCS which should

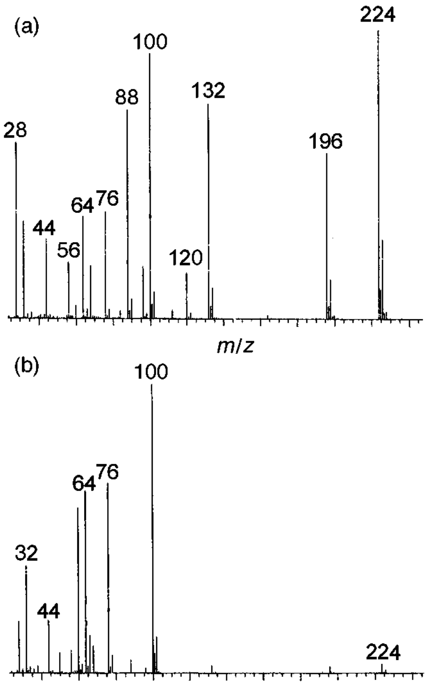


Fig. 3 EIMS of the thioxodithiolodithiolone **4** at two oven temperatures: (a) 200 and (b) 750 °C

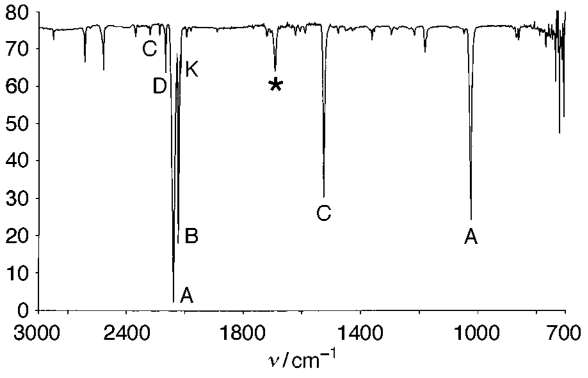
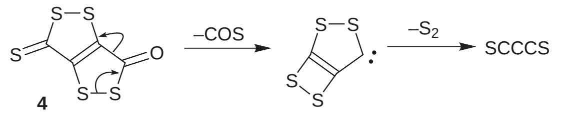


Fig. 4 IR spectrum (10 K argon matrix) of the pyrolysis products of compound **4** (1000 °C, 10^{-5} mbar). No significant peaks are present above 3000 cm^{-1}. Bands due to C_3S_2 (A) at 1024 and 2078 cm^{-1}, SCO (B) 2049 cm^{-1}, CS_2 (C) at 1527 and 2177 cm^{-1}, CO (D) at 2138 cm^{-1}, $S^{13}CC_2S$ (K) at 2031 cm^{-1} and unpyrolyzed starting material (*) are labelled.

show an absorption at 2209 cm^{-1} is not found. Carbon subsulfide formation is again rather pronounced in accordance with the favourable formation of a dithiete intermediate as shown in Scheme 3.



Scheme 3

Structure of the $[C_3S_2X]^{\cdot+}$ (X = O, S) radical cations generated by dissociative ionization of 3 and 4

The CA spectrum of the *m*/*z* 116 ions derived from **3** [Fig. 5(a)] features intense peaks at *m*/*z* 88 (loss of CO), already observed without the collision gas, *m*/*z* 84 (loss of sulfur) and 64 ($S_2^{\cdot+}$ ions) are readily interpreted in terms of formation of radical cations presenting the OCCCSS connectivity. Two other intense peaks are nevertheless observed at *m*/*z* 56 (SCC ions) and 44 (CS ions), peaks unexpected for such a connectivity. They may arise from consecutive dissociations of the *m*/*z* 88 fragments. An MS/MS/MS experiment performed on these ions, which are expected to be CCSS ions, is however not straightforward, the spectrum being quite similar to the CA spectrum of SCCS ions[12a,18] albeit a slight intensity increase of the loss of sulfur is noticed in the former case. As these *m*/*z* 88 ions are also formed from the metastable molecular ions, the loss of CO can be the result of a rearrangement reaction with production of ethenedithione, SCCS, ions.

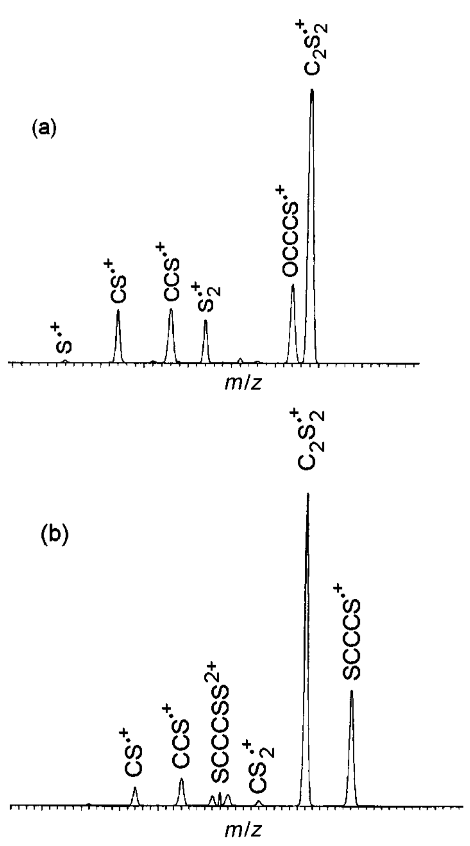


Fig. 5 CA (He) spectra of *m*/*z* 116 ion (a) and *m*/*z* 132 ion (b) observed in the EIMS of the dithiolodithioledione **3** and the thioxodithiolodithiolone **4**

Decarbonylation is the lowest energy decomposition pathway of the metastable molecular ions $\mathbf{4}^{\cdot+}$ and the resulting *m*/*z* 196 ions are responsible for the consecutive production of *m*/*z* 132 ions. The high energy CA of these species [Fig. 5(b)] suggests the SCCCSS connectivity by the intense peaks at *m*/*z* 100 (loss of sulfur) and 88 (loss of CS). In the present case, the other smaller peaks in the CA spectrum are also in agreement with the proposed SCCCSS connectivity.

Since the recent modification of our tandem sector mass spectrometer into a hybrid mass spectrometer (see Experimental section), it has been found on some occasions that the low energy CA spectra can be more structure specific than the corresponding high energy CA spectra.[19] That may be partly due to a lower energy deposition into the ions reducing the extent of consecutive fragmentations. Apart from the unimolecular fragmentations yielding *m*/*z* 88 ions, the CA (argon collision gas) spectra recorded at *ca.* 20–30 eV of the OCCCSS and the SCCCSS ions (from **3** and **4** respectively) feature only two peaks at *m*/*z* 64 (63%) and 84 (37%) (in the case of **3**) and *m*/*z* 64 (11%) and 100 (89%) (in the case of **4**). The OCCCSS and SCCCSS ions present therefore a common behaviour in these collision conditions (loss of sulfur and formation of disulfur ions) in keeping with the proposed cumulenic structures. It is worth noting that an intense loss of sulfur was seen in the CA spectra of similar 'dipole' ions like nitrile *N*-sulfides.[20]

Further evidence for the proposed structures has been found in ion–molecule reactions between decelerated OCCCSS and SCCCSS ions and nitric oxide. Fig. 6(a) and (b) show the result

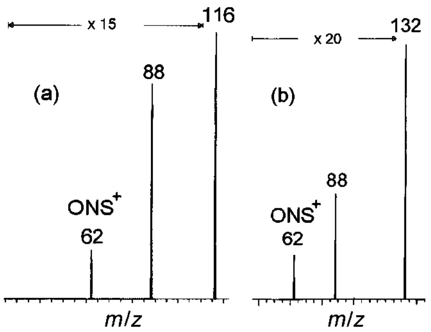


Fig. 6 Ion–molecule reactions between the *m*/*z* 116 ions of **3** (a) and *m*/*z* 132 ions of **4** (b) and nitric oxide

of such an interaction in a radiofrequency-only quadrupole collision cell giving rise to *m*/*z* 62 ions corresponding to ONS$^+$ cations. Such a behaviour has been interpreted as strong evidence for the occurrence of distonic ions in a number of cases.[21–23] Moreover, the main product of the reaction of SCSS ions (prepared by self-chemical ionization of carbon disulfide) with NO$^\bullet$ is also the formation of ONS$^+$ ions.[24]

Although the present experiments strongly support the generation of *S*-sulfide ions derived from OCCCS and SCCCS, the contribution of isomeric OCCC(S)S and SCCC(S)S ions cannot be completely excluded. This kind of ambiguous situation was also noticed for the lower homologue ions, SCSS and SC(S)S ions which are hardly differentiated in mass spectroscopic experiments.[25,26] Theoretical calculations have nevertheless predicted a higher stability of the SCSS ions compared to the SC(S)S ions[26] and such an order of stability should probably also apply for the present cumologue ions.

Experimental

General

The FTIR and argon matrix isolation apparatus employing a quartz thermolysis tube (150 mm length and 8 mm internal diameter) has been described earlier.[7] BaF$_2$ optics were used. The FVP/MS equipment, based on a six-sector tandem mass spectrometer (Micromass AutoSpec 6F) fitted with a quartz thermolysis tube (50 mm length, 3 mm inner diameter) directly connected to the outer ion source was as previously described.[27,28] Unless otherwise stated, the CA spectra were recorded by scanning the field of the second electric sector and collecting the ions with the first off-axis photomultiplier detector, the collision gas being helium. In its hybrid configuration, the AutoSpec 6F mass spectrometer was equipped with a radiofrequency-only quadrupole collision cell fitted with deceleration and reacceleration lenses;[29] such an arrangement allows the recording of spectra of slow ions and the study of ion–molecule reactions.

Materials

The samples of 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3,6-dithione (**2**),[30] 6-thioxo-3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]-dithiol-3-one (**4**)[30] and 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]-dithiole-3,6-dione (**3**)[31] were prepared according to literature procedures.

Conclusions

Cumulenes having an even number of carbons are less stable than their analogues possessing an odd number of carbons. The difference in stability is reduced for the corresponding radical-cations and that may explain the behaviour of the title compounds which, upon FVP, preferentially produce carbon subsulfide. Upon dissociative ionization of **3** and **4**, new sulfides of SCCCS and SCCCO are formed and characterized by collisional activation in the high or low kinetic energy regime and by ion–molecule reactions with nitric oxide. Theoretical calculations are in progress in order to support the proposed structures and to evaluate the stability of the corresponding neutral dipoles.

Acknowledgements

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References

1 D. Sülzle, *Phosphorus Sulfur*, 1993, **74**, 295.
2 D. Sülzle and H. Schwarz, *NATO ASI, Ser. C*, 1991, 237; *Chem. Abstr.*, 1992, **116**, 203 753.
3 C. O. Kappe, C. Th. Pedersen, J.-M. Catel and Y. Mollier, *J. Chem. Soc., Perkin Trans. 2*, 1994, 351.
4 M. W. Wong, C. Wentrup and R. Flammang, *J. Phys. Chem.*, 1995, **99**, 16 849.
5 C. Th. Pedersen, *Tetrahedron Lett.*, 1996, **37**, 4805.
6 T. Jørgensen, C. Th. Pedersen, R. Flammang and C. Wentrup, *J. Chem. Soc., Perkin Trans. 2*, 1997, 173.
7 R. Flammang, M. Barbieux-Flammang, P. Gerbaux and C. Th. Pedersen, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1261.
8 For a recent review, see: N. Golberg and H. Schwarz, *Acc. Chem. Res.*, 1994, **27**, 347.
9 D. Sülzle, N. Beye, E. Fanghänel and H. Schwarz, *Chem. Ber.*, 1990, **123**, 2069.
10 D. Sülzle and H. Schwarz, *Chem. Ber.*, 1989, **122**, 1803.
11 R. Flammang and C. Wentrup, *Sulfur Reports*, 1997, **20**, 255.
12 See for instance: (*a*) C. Wentrup, P. Kambouris, R. A. Evans, D. Owen, G. Macfarlane, J. Chuche, J. C. Pommelet, A. Ben Cheick, M. Plisnier and R. Flammang, *J. Am. Chem. Soc.*, 1991, **113**, 3130; (*b*) R. Flammang, S. Laurent, M. Flammang-Barbieux and C. Wentrup, *Rapid Commun. Mass Spectrom.*, 1992, **6**, 667; (*c*) R. Wolf, S. Stadtmüller, M. W. Wong, M. Barbieux-Flammang, R. Flammang and C. Wentrup, *Chem. Eur. J.*, 1996, **2**, 1318.
13 G. Maier, J. Schrot, H. P. Reisenauer and R. Janoschek, *Chem. Ber.*, 1991, **124**, 2617.
14 G. A. McGibbon, J. Hrusak, D. J. Lavorato, H. Schwarz and J. K. Terlouw, *Chem. Eur. J.*, 1997, **3**, 232.
15 G. Maier, J. Endres and H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1709.
16 A. J. Arduengo, J. R. Goerlich and W. J. Marshall, *Liebigs Ann. Chem.*, 1997, 365.
17 C. Th. Pedersen, J. Oddershede and J. Sabin, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1062.
18 D. Sülzle and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1337.
19 P. Gerbaux, R. Flammang, M. T. Nguyen, J. Y. Salpin and G. Bouchoux, *J. Chem. Phys. A*, 1998, **102**, 861.
20 R. Flammang, P. Gerbaux, E. H. Mørkved, M. W. Wong and C. Wentrup, *J. Phys. Chem.*, 1996, **100**, 17 452.
21 T. Weiske, H. van der Wel, N. M. M. Nibbering and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 733.
22 P. Gerbaux, R. Flammang, E. H. Mørkved, M. W. Wong and C. Wentrup, *Tetrahedron Lett.*, 1997, **32**, 503.
23 R. Flammang, M. Barbieux-Flammang, P. Gerbaux, C. Wentrup and M. W. Wong, *Bull. Soc. Chim. Belg.*, 1997, **106**, 545.
24 P. Gerbaux and R. Flammang, unpublished results.
25 D. Sülzle, H. Egsgaard, L. Carlsen and H. Schwarz, *J. Am. Chem. Soc.*, 1990, **112**, 3750.
26 P. Gerbaux, Y. Van Haverbeke, R. Flammang, M. W. Wong and C. Wentrup, *J. Phys. Chem. A*, 1997, **101**, 6970.
27 R. H. Bateman, J. Brown, M. Lefevere, R. Flammang and Y. Van Haverbeke, *Int. J. Mass Spectrom. Ion Processes*, 1992, **115**, 205.
28 J. Brown, R. Flammang, Y. Govaert, M. Plisnier, C. Wentrup and Y. Van Haverbeke, *Rapid Commun. Mass Spectrom.*, 1992, **6**, 249.
29 R. Flammang, Y. Van Haverbeke, C. Braybrook and J. Brown, *Rapid Commun. Mass Spectrom.*, 1995, **9**, 795.
30 B. Kordts, A. M. Richter and E. Fanghänel, *Monatsh. Chem.*, 1991, **122**, 71.
31 A. M. Richter and E. Fanghänel, *Tetrahedron Lett.*, 1983, **24**, 3577.

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