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THERMOLYSIS OF 1,2-DITHIOLYLIUM SALTS IN THE ION SOURCE OF THE MASS SPECTROMETER

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Abstract—1,2-Dithiolylium salts are thermolysed in the ion source of a mass spectrometer; some salts (group I) undergo thermolysis to give a stable dithiolyl radical where subsequent ionization gives rise to a mass spectrum in which the parent ion corresponds to the dithiolyl ion. The radical may be stabilized before ionization by expulsion of a hydrogen atom to form a neutral dithiole derivative, and then mass spectra exhibit abundant molecular ions corresponding to such dithiole derivatives.

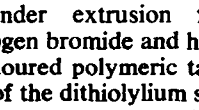
Other salts (group II) may expel a proton with formation of a carbene and subsequent dimerization to a tetrathiafulvalene.

The thermolytic behaviour of 1,2-dithiolylium salts is compared with their electrochemical behaviour and several analogies are found.

INTRODUCTION

We have previously studied the mass spectrometric fragmentation of 1,2-dithiol-3-thiones, 1,2-dithiol-3-ones, 1,6,6AIVS-trithiapentalenes, 1,2-dithiolylidene ketones and aldehydes and multisulfur systems related to the 1,2-dithiole system.[1-4]

As simple 1,2-dithiole derivatives without an electronegative bivalent group in the 3-position are unknown,[5] the only known systems which have the 1,2-dithiole nucleus with simple substituents are the 1,2-dithiolylium salts **A**.



A

The dithiolylium salts are true ionic non-volatile salts.[6] Upon heating in hydrocarbon suspension (benzene, toluene, xylene and mesitylene) they are thermolyzed under extrusion from e.g. the bromides, hydrogen bromide and hydrogen sulfide, leaving dark coloured polymeric tars.

Introduction of the dithiolylium salts into the ion source of the mass spectrometer by means of the direct insertion probe and subsequent heating of the sample to 150–200°C gave rise to characteristic and reproducible spectra. An examination suggested that the spectra could be due to the thermolysis products. Although too unstable to be isolated, these thermolysis products may have a lifetime sufficient to allow ionization by electron impact, when formed directly in the ionization chamber. Thus this technique makes it possible to study the primary thermolysis products.

Application of mass spectrometry to iso-π-electronic pyrylium salts has been reported.[7] However, in this study the spectra obtained were considered as mass spectra of the salts which implies the existence of the salts in the vapour phase. In our study of 1,2-dithiolylium salts no trace of molecular ions corresponding to the parent salts could be observed as was also reported to be the case for 1,2,3-triphenyl cyclopropenium bromide,[8] and the pyrylium salts.[7] Thus it seems better to consider the mass spectra of 1,2-dithiolylium salts and pyrylium salts as spectra of the thermolysis products.

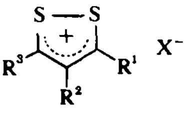
The present study makes use of bromides although from a preparative point of view the perchlorates are more convenient. The perchlorates are more ionic than the bromides but require a higher thermolysis temperature which in most cases is accompanied by secondary processes, e.g. dimerisation and desulfurisation. For these reasons the present study concentrates on ions which give crystalline bromides. However, a perchlorate and an iodide have also been included. The use of chlorides instead of bromides resulted in completely identical spectra, except for the halogen containing ions.

The compounds studied are shown in Table 1.

RESULTS

The results from the mass spectrometric study may be rationalized by the following two reaction

Table 1.

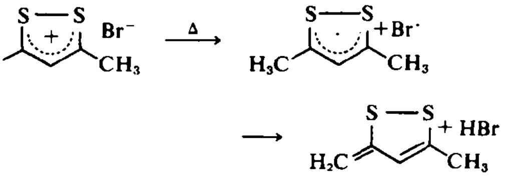


	R¹	R²	R³	X
1	CH_3	$CH_2(CH_2)_2CH_2$		Br
2	C_2H_5	$CH_2(CH_2)_2CH_2$		Br
3	C_6H_5	$CH_2(CH_2)_2CH_2$		Br
3a	C_6D_5	$CH_2(CH_2)_2CH_2$		Br
4	CH_3	$CH_2(CH_2)_3CH_2$		Br
5	CH_3	$CH_2(CH_2)_8CH_2$		Br
6	C_2H_5	$CH_2CH_2CH_2$		Br
7	CH_3	H	CH_3	Br
8	CH_3	CH_3	CH_3	Br
9	CH_3	H	C_6H_5	Br
10	H	H	H	J
11	$C(CH_3)_3$	H	$C(CH_3)_3$	ClO_4
12	C_6H_5	H	C_6H_5	Br
13	C_6H_5	H	H	Br
14	H	C_6H_5	H	Br
15	C_6H_5	C_6H_5	H	Br

pathways for the primary thermolysis processes (**1** and **2**).

I *Primary formation of a dithiolyl radical*

The mass spectra exhibited by **10**, **11**, and **12** show abundant parent ions corresponding to ionized dithiolyl radicals. In the cases of **1** to **11** the primary formed radicals are too short-lived to be ionized. Their mass spectra show abundant molecular ions corresponding to dithiole derivatives formed by loss of a hydrogen atom from the dithiolyl radicals (Scheme 1). Formally, this reaction pathway corresponds to the loss of hydrogen bromide from the parent salt; [HBr] ions give rise to intense peaks in all bromide spectra.



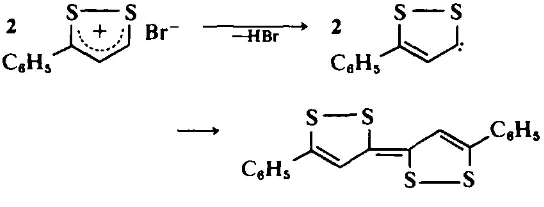
SCHEME 1

Results obtained from cathodic reduction of dithiolylium salts are consistent with these observations. It was shown[9,10] that, in the absence of reactive species, the radicals formed from **11** and **12** possess a high stability. In all other cases investigated the electrochemistry was in accordance with the formation of a dimer.

Thermolysis at higher ion source temperature in some cases gave rise to mass spectra which were in accordance with the formation of dimers.

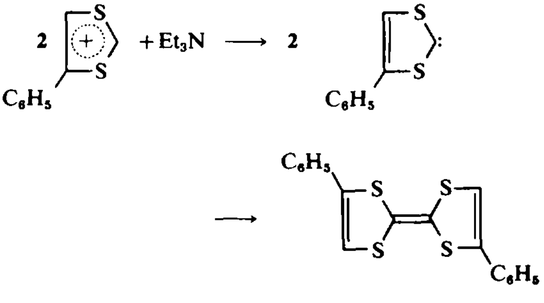
II *Loss of a proton from the dithiolylium ion*

Compounds **13**, **14** and **15** exhibit spectra which may indicate the presence of a tetrathiafulvalene. A possible formation, involving the loss of a proton from the dithiolylium ion with formation of a carbene and subsequent dimerization, is shown in Scheme 2.



SCHEME 2

It is known in the 1,3-dithiole series that weak bases such as triethylamine can split off a proton from 1,3-dithiolylium salts giving rise to the formation of stable dimers, probably via carbenes. (*cf* Ref 11 and references given there).



This reaction fails in the 1,2-dithiole series[12] and it has not been possible to generate tetrathiafulvalenes electrochemically,[13,14] although this does not exclude the formation of tetrathiafulvalenes under the condition used in this study.

DISCUSSION

As a consequence of the different thermal fragmentation modes, **1** and **2**, we will consider the dithiolylium salts under investigation in two classes.

Class I

The mass spectra of the thermolysis products exhibited by the compounds in which the dithiol moiety is condensed with a cycloalkane ring (**1** to **6**) are shown in Fig 1. The molecular ions correspond to the loss of hydrogen bromide from the parent salt and give rise to the base peak in all cases. Their fragmentation is similar with loss of a hydrogen atom and a methyl group being a characteristic feature. This may suggest that the hydrogen atom originally lost in the thermolysis process of the parent salt is expelled from similar positions.

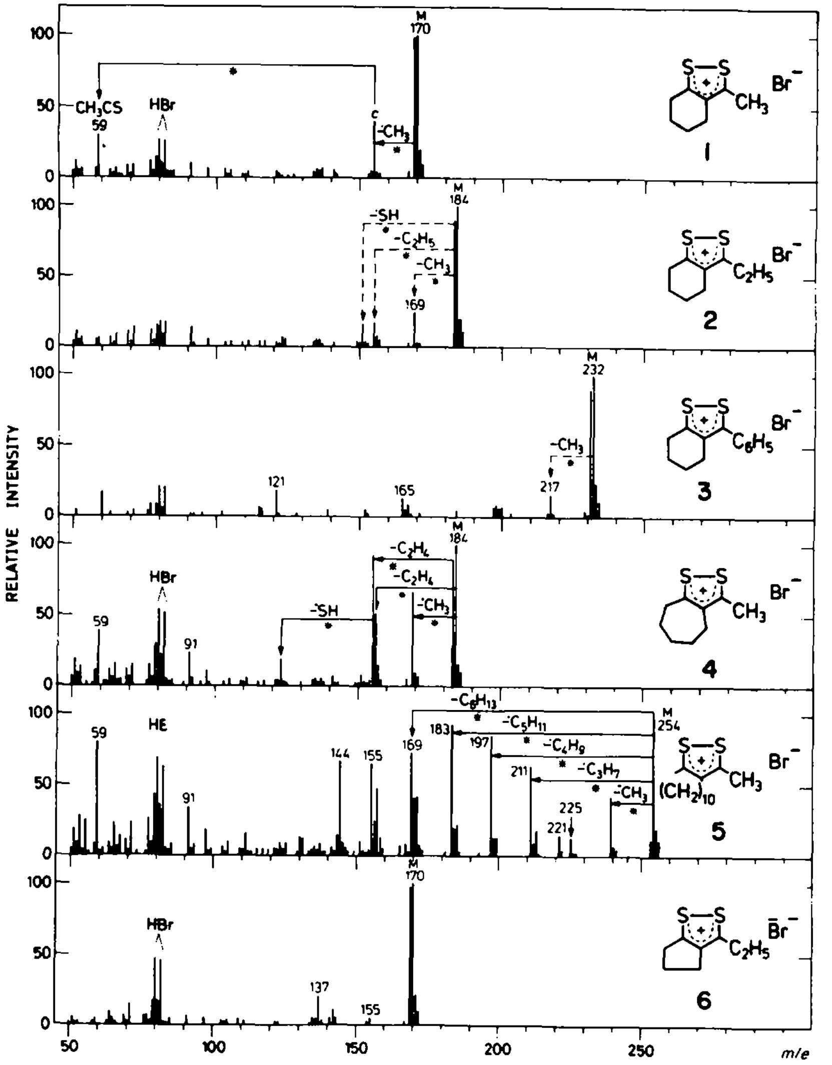
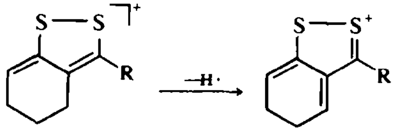


Fig 1.

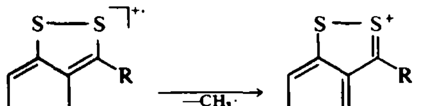
Reasonable structures for the molecular ions may be **a**, which allows the [M-H] ions to be formulated as **b**.



M: **a** M—H: **b**

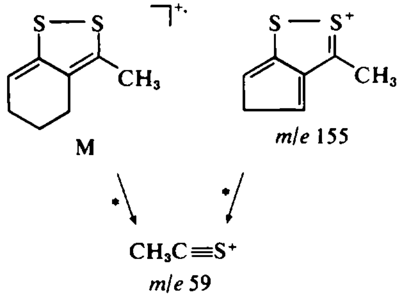
Corresponding structures may be written for **4**, **5** and **6**. The formulation of **a** is in agreement with the spectrum exhibited by **3a** ($R = C_6D_5$) in which all labelled hydrogens are retained in the molecular ion. Structure **b** is consistent with the appearance of a [M-1] peak. The presence of a [M-2] peak, however, indicates that a hydrogen atom is lost from the phenyl group as well (the [M-D] peak has half the intensity of the [M-H] peak).

Ions corresponding to the loss of $\cdot CH_3$ from the molecular ions give rise to important peaks in most of the spectra. The loss of ·R from **a** may contribute to this [M-CH_3] ion in the cases where $R = CH_3$, since corresponding [M-C_2H_5] ions are formed when $R = C_2H_5$ (**2** and **6**). However, since the spectra of **3** ($R = C_6H_5$) and **3a** ($R = C_6D_5$) exhibit the loss of a $\cdot CH_3$ group as well, the following reaction may take place yielding the [M-CH_3] ion as **c**:



M M−15: **c**

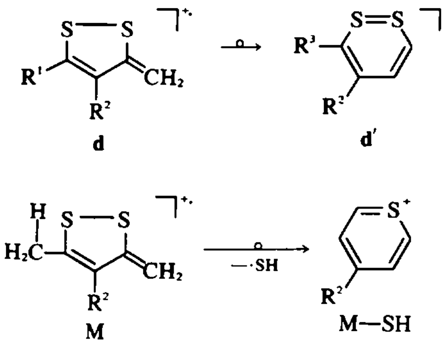
This process, involving the loss of ·CH_3 from the condensed ring system, is consistent with the more abundant [M-CH_3] ion in **2** relative to **6**. Furthermore *m/e* 155 (**c**) is a precursor (together with the molecular ion) for the [CH_3CS] ion (*m/e* 59) as shown in the case of **1** from a study of metastable ions.



The abundant ion at *m/e* 155 in the spectra of **4** and **5** may also be assigned structure **c**. In **4** the *m/e* 155 ion is formed by loss of C_2H_4 from the [M-H] ion and by loss of H from the [M-C_2H_4] ion, and is also in this case progenitor for the [CH_3CS] ion. Electron-impact-induced loss of ·CH_3 from cyclohexene is a well known process.[15] In this case where the cyclohexene ring is condensed with the dithiole moiety a simultaneous ring contraction may take place.

The spectra of the non annelated salts **7** to **9** are shown in Fig 2.

The molecular ions correspond to the thermal loss of hydrogen bromide from the parent salt. The molecular ions may be assigned the general structure **d** (or the rearranged **d'**), supporting the preferred loss of ·SH from the molecular ions of **7** and **8** but not from **9**, by the following process:



All three molecular ions expel S_2 and ·HS_2. **7** and **8** form the [CH_3CS] ion (*m/e* 59), while **9** exhibits *m/e* 121 (C_6H_5CS).

The mass spectra exhibited by **10**, **11** and **12** (Fig 3) are consistent with the interpretation that the parent ions are due to the free dithiolyl radicals formed in the thermolysis processes in the ion source. Ionization of these radicals will give rise to the highly stable aromatic 1,2-dithiolylium cations. This explains the high abundance of these ions. Only little fragmentation is shown in the case of **10** and **12**, while the presence of the tert-butyl groups in **11** gives rise to increased fragmentation. As the bromide of di-tert-butyl-1,2-dithiolylium ion was not crystalline, the perchlorate had to be used. Although an ion source temperature of 200–250° was necessary to obtain thermolysis, the parent ion still correspond to the dithiolyl radical.

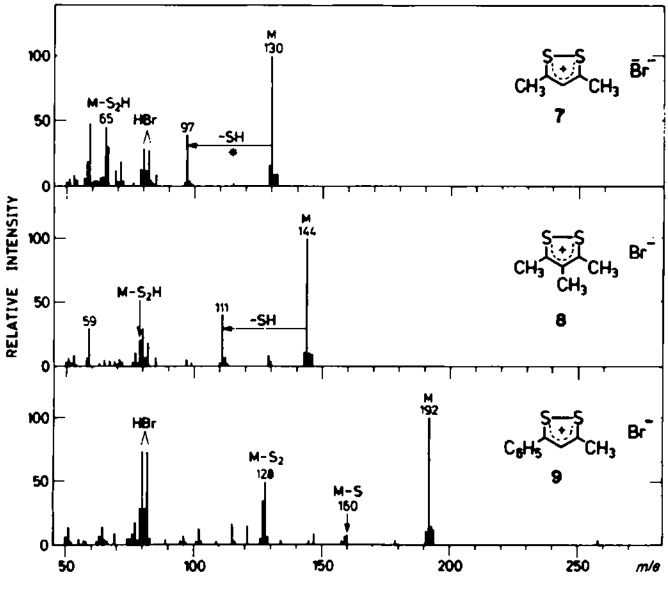


Fig 2.

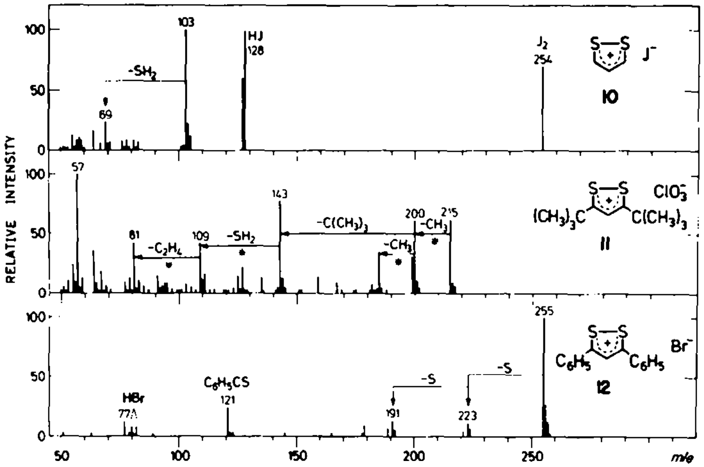
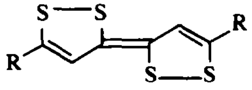


Fig 3.

Class II

The mass spectra obtained from **13–15** did not give any indications of the formation of a dithiolyl radical or a dithiole derivative corresponding to loss of hydrogen bromide from the parent salt. If the spectra were recorded at low temperature only peaks corresponding to hydrogen bromide were recorded.

The mass spectra which appeared at higher temperatures (Fig 4) may be due to tetrathiafulvalenes (**B**) and to their thermolysis products, formed by loss of one or two sulfur atoms.



B

Loss of one and two sulfur atoms and of H_2S_2 and

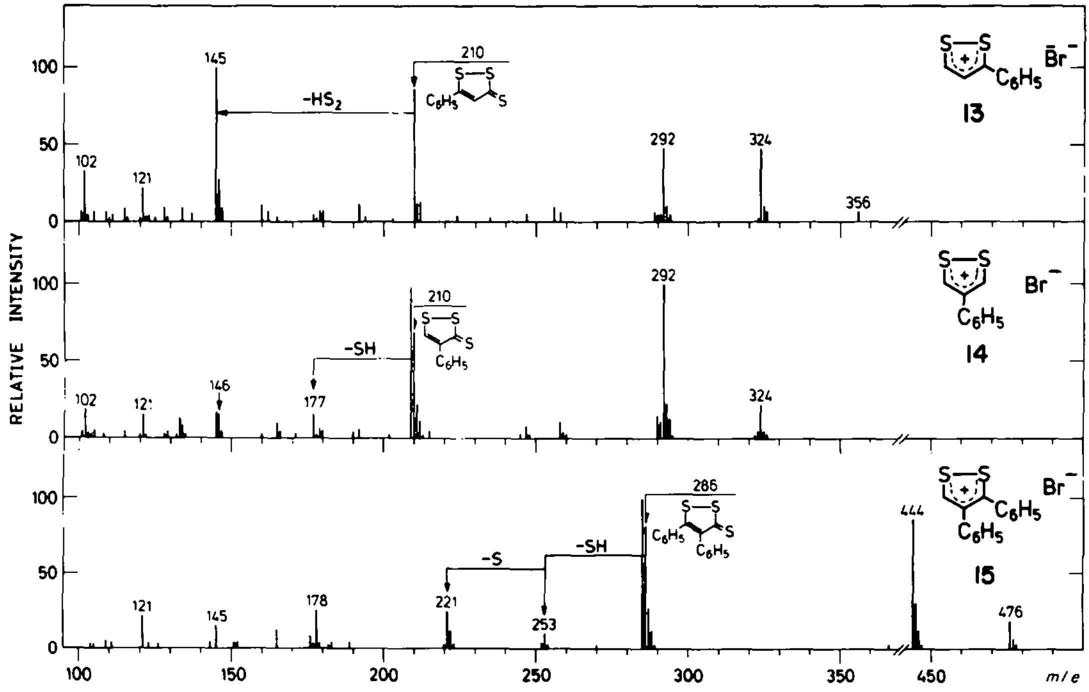
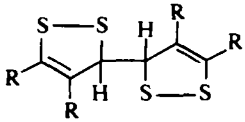


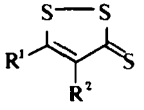
Fig 4.

H_2S has also been observed in dihydro tetrathiafulvalenes C.[16]



C

Furthermore, an indication for the formation of substituted 1,2-dithiole-3-thiones D during the thermolysis was found.



D

The characteristic electron-impact-induced fragmentation of the phenyl substituted 1,2-dithiole-3-thiones[1] can be recognized in the spectra, and application of the metastable defocusing technique on the 1,2-dithiole-3-thione ions supports the thermal origin for these compounds as no precursors could be found.

It is a well known observation, that 1,2-dithiolylium salts react with elementary sulfur under very mild condition forming 1,2-dithiol-3-thiones.[17] We will therefore assume that sulfur formed by thermal degradation of the dithiolylium salt in the ion source reacted with dithiolylium salts and has given rise to these compounds.

EXPERIMENTAL

The mass spectra were obtained on a MS 902 mass spectrometer using the direct sample insertion system with a sample probe of pyrophylite and the lowest feasible ion source temperature (120–250°C). 70 eV electrons were used. Peaks corresponding to doubly charged ions appearing at half mass numbers and peaks of abundance lower than 2% were omitted.

Dithiolylium salts. 2-Monoaryl-, and 3,4-diaryl-substituted salts were prepared by oxidation of the corresponding 1,2-dithiole-3-thiones.[18] Unsubstituted, 3,5-disubstituted, and trisubstituted salts were prepared from the appropriate β dicarbonyl compounds and diacetyl disulfide.[19] The dithiolylium salts were characterized as their perchlorates. All compounds showed satisfactory analysis.

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