

Thermolytic Fragmentation of 3-Alkylthio- and 3-Arylthio-1,2-dithiolylium Iodides in the Ion Source of the Mass Spectrometer

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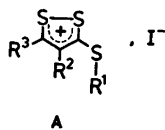
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A series of 3-alkylthio- and 3-arylthio-1,2-dithiolylium iodides have been thermolysed in the ion source of the mass spectrometer. The mass spectra obtained from the thermolysis products of the alkylthio substituted compounds can be rationalized by assuming the primary formation of a 1,2-dithiolyly radical. The radical may stabilize either by loss of the thioalkyl alkyl group or by loss of a hydrogen atom.

The 3-arylthio substituted compounds form a tetrathiafulvalene, probably by dimerization of an intermediately formed carbene.

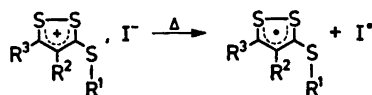
A mass spectrometric study of the thermolysis products of alkyl- and aryl substituted 1,2-dithiolylium salts has recently been reported.¹ Although some of the thermolysis products are not stable enough to be isolated, they are sufficiently long lived to allow ionization by electron impact when formed directly in the ionization chamber. Thus mass spectra obtained in this way make it possible to study the primary thermolysis products or the primary rearrangements products.

In this investigation salts of the type (A) (Table 1) were studied under the same conditions as before.¹

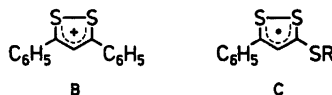


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The mass spectra of the various thermolysis products may be rationalized by assuming the primary formation of a 1,2-dithiolyly radical by a sort of homolytic cleavage (I—XIII).



An analogous process was proposed as the primary process in the thermolysis of alkyl- and aryl substituted 1,2-dithiolylium salts,¹ where the thermolysis in some cases, *e.g.* 3,5-diphenyl-1,2-dithiolylium bromide, gave rise to the formation of stable radicals. Subsequent ionization then yielded the stable aromatic 1,2-dithiolylium cation (B) as the very abundant parent ion in the mass spectrum.



Similar abundant ions corresponding to radicals as (C) are not observed in any of the mass spectra from the salts studied in this investigation. However, the spectra from alkylthio dithiolylium salts bearing an aromatic substituent (IX—XIII) exhibit, besides the spectrum of the thermolysis product, an ion of low abundance (0.1—2 %) at a *m/e* value corresponding to the appropriate radical. Such peaks could not be detected in the spectra of I to VIII since the *M* + 1 isotope peaks of the abundant molecular

Table 1. Salts of type (A).

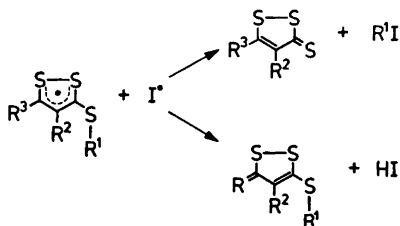
	R ¹	R ²	R ³	M.p., °C ^a
I	CH ₃	H	CH ₃	
II	CD ₃	H	CH ₃	
III	CH ₃	CH ₃	CH ₃	
IV	C ₂ H ₅	CH ₃	CH ₃	153–155
V	CH ₃	–CH ₂ –CH ₂ –CH ₂ –		
VI	CD ₃	–CH ₂ –CH ₂ –CH ₂ –		162–165
VII	CH ₃	–CH ₂ –CH ₂ –CH ₂ –CH ₂ –		148–149
VIII	CD ₃	–CH ₂ –CH ₂ –CH ₂ –CH ₂ –		147–148
IX	CH ₃	C ₆ H ₅	H	
X	C ₂ H ₅	C ₆ H ₅	H	174–176
XI	CH ₃	H	C ₆ H ₅	
XII	C ₂ H ₅	H	C ₆ H ₅	
XIII	CH ₃	C ₆ H ₅	C ₆ H ₅	
XIV	C ₆ H ₅	H	C ₆ H ₅	

^a All compounds melt with decomposition.

ion of the decomposition product appear at the same nominal mass number.

The observations described above are in accordance with the electrochemical behaviour of the two groups of salts. The 3,5-diphenyl-1,2-dithiolylium perchlorate gave reversible electrochemistry at room temperature and the corresponding stable radical was characterized by means of ESR spectroscopy.² 3-Methylthio-5-phenyl-1,2-dithiolylium methosulfate showed reversible electrochemistry only at $-70\text{ }^{\circ}\text{C}$ ³ indicating the lower stability of the radical.

The primary rearrangement process of the radicals initially formed from the alkylthio substituted salts could proceed in two different ways as suggested in Scheme 1.



Scheme 1.

Loss of the thioalkyl group R¹

The mass spectra exhibited by IX to XIII show abundant molecular ions corresponding to alkyl iodides and the appropriate 1,2-dithiol-3-

thiones. The fragmentation patterns of the latter are virtually identical with those previously reported for these compounds.⁴ This process accounts for all significant peaks observed in the spectra.

Loss of the alkyl group R¹ is also observed in the spectra of I to VIII, but to a much smaller extent.

Loss of a hydrogen atom

The major rearrangement process of the initially formed radicals in the case of compounds I to VIII corresponds to the initial loss of a hydrogen atom (Scheme 2). The mass spectra show the resulting [HI]⁺ ion and abundant molecular ions corresponding to loss of hydrogen iodide from the parent salt (*cf.* Figs. 1 and 2). The hydrogen atom involved in this process do not originate from the alkylthio group R¹, as demonstrated by the spectra obtained from the deuterated salts II, VI, and VIII. In these cases all labelled hydrogens are retained in the molecular ions.

The mass spectrum exhibited by VII is shown in Fig. 1. A reasonable structure for the molecular ion appearing at m/e 202 may be α . This is in accordance with the structure proposed for the thermolysis product obtained from 3-methyl-4,5-tetramethylene-1,2-dithiolylium bromide.¹ Similarly the [M–H] ion is

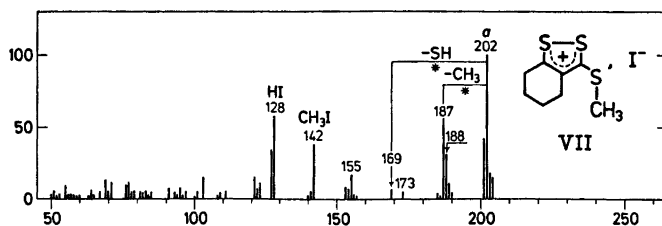
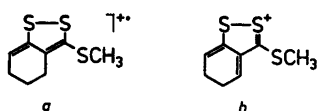


Fig. 1.



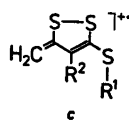
designated structure *b*, which is consistent with the spectrum of the deuterium labelled compound VIII.

The ion corresponding to the loss of $\cdot\text{CH}_3$ from the molecular ion gives rise to the abundant peak at m/e 187. Loss of methyl from the condensed ring system leading to a ring contraction as suggested for 3-methyl-4,5-tetramethylene-1,2-dithiolylium bromide¹ may also take place here. However, the alkyl group R^1 is lost preferentially, since in the spectrum of VIII the peak corresponding to the loss of CD_3 is five times as abundant as that corresponding to the loss of CH_3 .

The hydrogen atom involved in the $\cdot\text{SH}$ loss preferentially originates from the condensed system.

The peak at m/e 188 corresponds to the molecular ion of 4,5-tetramethylene-1,2-dithiol-3-thione most likely formed by loss of the alkyl group R^1 from the primary radical, Scheme 1. Loss of $\cdot\text{CH}_3$ and $\cdot\text{SH}$ from m/e 188 give rise to the ions at m/e 173 and 155, respectively, as was also observed for an authentic sample of 4,5-tetramethylene-1,2-dithiol-3-thione.⁵

The structure of the molecular ion observed in the mass spectra obtained from I to IV corresponds to the loss of a hydrogen atom from the methyl group in the 5 position of the initially formed radical. This process yielding *c* is analogous to the formation of *a*, and is in

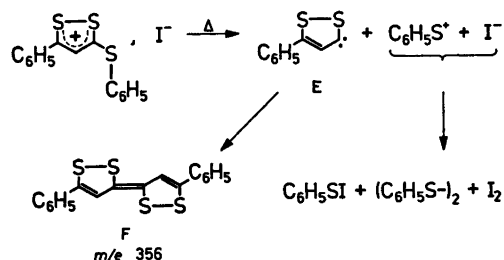


accordance with calculations of the spin densities in the dithiolylium radical.^{6,7} These calculations suggest a high spin density in the 3 and 5 positions which will facilitate the loss of a hydrogen atom from the methyl group in the 5 position.

The mass spectrum of compound I is typical for this group and is shown in Fig. 2. Loss of R^1 and SR^1 from the molecular ion are characteristic processes. If the salt is unsubstituted in the 4 position, *e.g.* I, the molecular ion shows the loss of $\cdot\text{S}_2\text{H}$ whereas III and IV with a methyl group in the 4 position expel $\cdot\text{SH}$ from the molecular ions. These differences in fragmentation are the same as found for 4-methyl-1,2-dithiol-3-thione and 5-methyl-1,2-dithiol-3-thione.⁴ The peaks at m/e 83 and 71 are due to the loss of S_2 and CS_2 , respectively, from the $[\text{M} - \text{R}^1]$ ion. Corresponding peaks are found in the other cases too.

The mass spectrum of the phenylthio compound XIV indicates a somewhat different thermolytic behaviour than that observed for the alkylthio substituted compounds.

The spectrum of XIV exhibits the base peak at m/e 109, which corresponds to $\text{C}_6\text{H}_5\text{S}$. This fragment is probably formed by a heterolytic cleavage (Scheme 2) and before ionization $\text{C}_6\text{H}_5\text{SI}$ and $\text{C}_6\text{H}_5\text{S} - \text{SC}_6\text{H}_5$ are formed by nu-



Scheme 2.

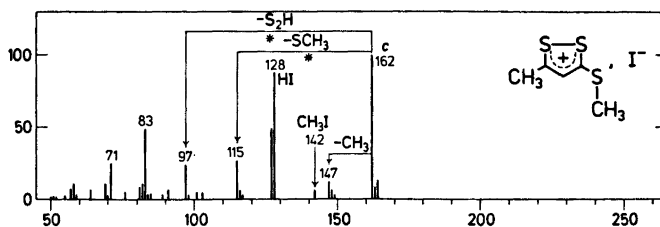
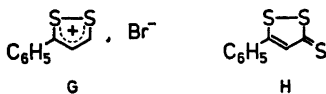


Fig. 2.

cleophilic attack of the iodide ion on $C_6H_5S^+$ and by reduction of this ion by I^- . The phenyl sulfenyl iodide and the diphenyl disulfide give rise to intense peaks at m/e 236 and m/e 218, respectively. Intense peaks corresponding to $[I]^+$, $[HI]^+$, and $[I_2]^+$ are also present.

The carbene formed by loss of $C_6H_5S^+$ dimerize prior to ionization accompanied by the formation of the tetrathiafulvalene (F). This behaviour is analogous to that previously reported for 5-phenyl-1,2-dithiolium bromide (G),¹ and the spectra obtained from XIV and (G) are very similar (apart from the iodine and C_6H_5S containing ions).

The fragmentation pattern of 5-phenyl-1,2-dithiol-3-thione (H) gives rise to abundant peaks in the spectrum of XIV. (H) may arise by a mechanism analogous to that depicted for the formation of 1,2-dithiol-3-thiones in Scheme 1. However, since no peak corresponding to $[C_6H_5I]^+$ is observed, a thermal mechanism similar to that proposed in the case of (G)¹ is considered to be more likely.



EXPERIMENTAL

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

*3-Alkylthio-1,2-dithiolium iodides** were prepared from the appropriate 1,2-dithiol-3-thiones and methyl iodide either in refluxing butyl acetate⁹ or in chloroform at room temperature.⁹

*3-Phenylthio-1,2-dithiolium iodide** was prepared as described by Faust *et al.*¹⁰

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