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Mass Spectra of Thioamides

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The mass spectra of various thioamides have been recorded and interpreted with the aid of exact mass measurements and metastable defocussing technique. Loss of a sulfhydryl radical from the molecular ions is generally an important process and may in some cases be taken as evidence for a strong enethiolization of the molecular ion.

Thiocarbonyl compounds investigated by mass spectrometry include thionoesters,[1,2] thiocarbonates,[1,3] thiocarbamates,[1,3] thioureas,[1,4–6] thiohydrazides, thiourethanes,[7] a few thioamides,[8,9] and various heterocyclic compounds.[10]

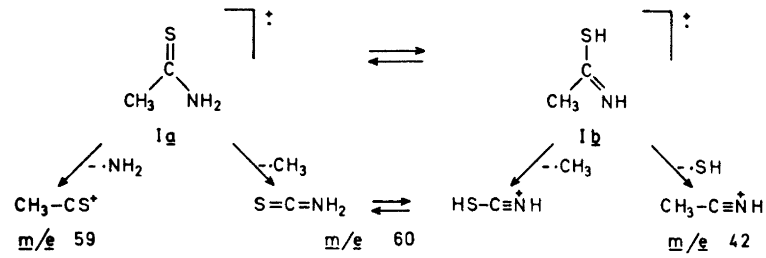
From our study of the mass spectra of various thioamides we here want to discuss the mass spectra of the following compounds:

I. Thioacetamide. II. Thiobenzamide. III. *o*-Methoxythiobenzamide. IV. *N*-Methylthiobenzamide. V. *N*,*N*-Dimethylthiobenzamide. VI. Thioacetanilide. VIII. *p*-Methylthioacetanilide. IX. *o*-Methyoxythioacetanilide.

RESULTS AND DISCUSSION

The mass spectrum (Fig. 1) of thioacetamide (I) displays an abundant molecular ion peak as expected for a small molecule. From the reported mass spectrum of acetamide [4,11] (Table 1) thioacetamide is expected to undergo α-cleavages upon electron impact.

This was also the case, as abundant peaks at *m/e* 60 and 59, corresponding to the loss of $\cdot CH_3$ and $\cdot NH_2$ from the molecular ion, are found, but in addition the mass spectrum of thioacetamide contains a 50 % peak at *m/e* 42 due to an M − ·SH ion. This decomposition can best be rationalized with the assumption of an initial "enethiolization" of the molecular ion prior to α-cleavage,[8] as depicted in Scheme 1.



Scheme 1.

Table 1. Comparison of the mass spectra of CH_3CONH_2 and CH_3CSNH_2.

Ion	CH_3CONH_2 %	CH_3CSNH_2 %
M	100	100
$M-CH_3$ (α_1)	76	71
$M-NH_2$ (α_2)	57	28
α_1/α_2	1.33	2.53

Whereas the abundance of the $M-\cdot CH_3$ ion is 1.33 times that of the $M-\cdot NH_2$ ion in the case of acetamide, the ratio is 2.53 in the case of thioacetamide, as seen from Table 1. This fact can be taken as evidence for an initial "enethiolization", as the ion I*b* is unable to undergo loss of $\cdot NH_2$, but it might also

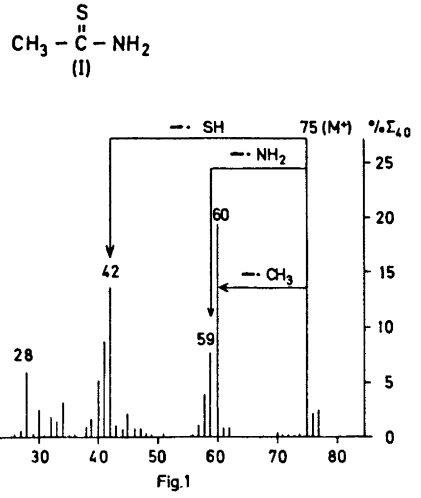
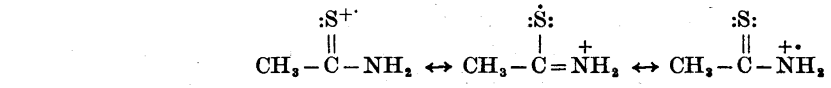


Fig.1

indicate a more pronounced interaction between the lone pair on the nitrogen atom and the double bond in the thioamide than in the amide. This interaction will lead to a delocalization of the charge as well as the unpaired electron, as described with the resonance structures:



The mass spectrum (Fig. 2) of thiobenzamide (II) has recently been published and discussed.[9] The more important fragmentation and rearrangement processes of thiobenzamide are depicted in Fig. 2. In connection with the discussion of the abundance of $M^{+\cdot} - \cdot CH_3$ ion *versus* that of the $M^{+\cdot} - \cdot NH_2$ ion from thioacetamide it should be noted that in the case of thiobenzamide loss of $\cdot NH_2$ is twice as important as the expulsion of $\cdot C_6H_5$, indicating the mesomeric interaction between the aromatic moiety and the CS group.

It has been suggested in the discussion of the mass spectrum of thiobenzamide by Holmes and Benoit [9] that the ion of mass 103 (corresponding in

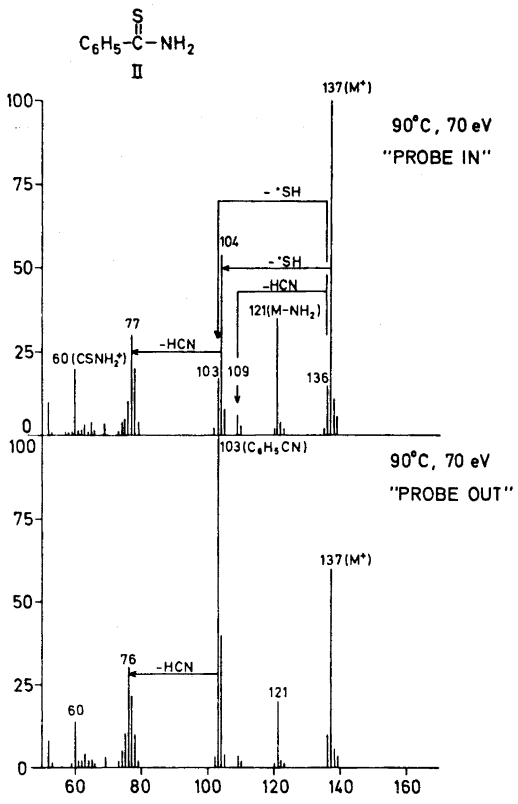


Fig. 2

composition – and most likely also in structure – to ionized benzonitrile) might be formed by the decomposition of $M^{+\cdot}$ by loss of H_2S and/or by the loss of a hydrogen atom from 104^+ ($M^{+\cdot} - \cdot SH$). We have, however, found certain indications for a thermal as well as an electron impact induced origin of this ion as stressed in the following paragraph.

The mass spectrum (Fig. 2) of thiobenzamide was recorded at two different sets of conditions. In both cases the direct insertion technique was applied. The mass spectrum marked "Probe in" was obtained with the probe right in the ionization chamber, whereas that marked "Probe out" was recorded with the probe pulled a distance back. In the first case the sample evaporized direct into the electron beam, in the latter the sample passes along the heated walls of the ion source increasing the possibility for thermal decomposition.

The formation of 104^+ from the molecular ion gives rise to a metastable peak at *m/e* 79.0, and this peak is retained even at 12 eV, whereas no metastable peaks indicating the formation of $103^{+\cdot}$ have been observed, neither at 70 eV nor at low voltages (20 – 12 eV). Application of the defocussing technique, however, revealed that the M – 1 ion is a precursor for $103^{+\cdot}$, clearly demonstrating the electron impact induced origin of the $M - H_2S$ ion.

That the ionized benzonitrile can also be due to a thermal degradation prior to ionization is clearly evidenced by the mass spectrum recorded with the probe a short distance apart from the electron beam. This spectrum is a superposition of the mass spectra of thiobenzamide and benzonitrile.

Introduction of substituents into the aromatic ring did surprisingly not lead to new electron impact induced processes. Out of the compounds investigated we here want to report our findings dealing with the mass spectrum of *o*-methoxythiobenzamide (III), as the methoxy group is known often to conduct the fragmentation pattern of aromatic compounds, and when situated in the 2-position to participate in "ortho-effect" reactions.

Skeletal rearrangements as those reported for 2-ethoxy benzamide [12] were not observed and the α-cleavages have become unimportant. The fragment

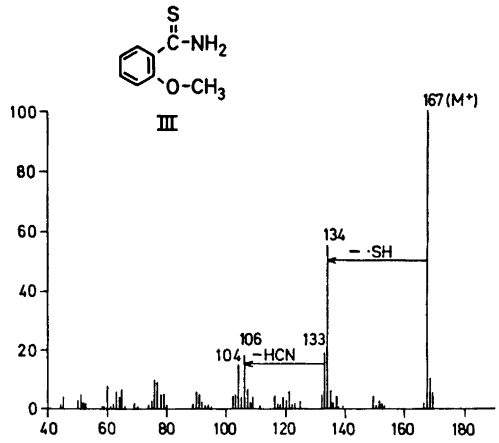


Fig. 3

ion peak of highest abundance is due to the loss of ·SH from the molecular ion.

In the mass spectrum (Fig. 4) of *N*-methylthiobenzamide (IV) the peak due to M − ·SH (*m/e* 118) is of less importance than in the preceding spectra. Two abundant peaks are found at *m/e* 150 (M − 1) and 121 ($C_6H_5CS^+$). The

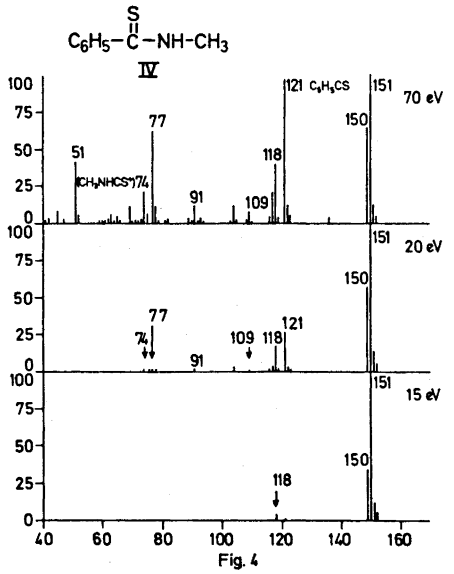
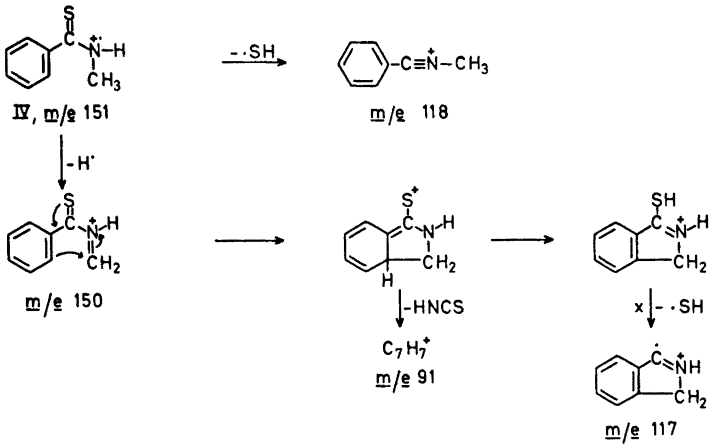


Fig. 4

mass spectrum of thiobenzamide contained an M − 1 peak, but it was only 17 % of the molecular ion peak, and the abundance decreased rapidly with the electron energy. In the mass spectrum of IV the M − 1 peak is 64 % of the molecular ion peak and it remains important at low voltage.[13] This mass spec-



Scheme 2.

trum also contains metastable peaks, corresponding to the loss of ·H from $M^{+\cdot}$ and the loss of ·SH from the M − 1 ion. Further, this spectrum as well as that of *N*,*N*-dimethylthiobenzamide (V, Fig. 5) contain peaks at *m/e* 91 corresponding to $C_7H_7^+$, whereas no such peak was found in the mass spectrum of thiobenzamide (II).

Assuming the formation of a bond between the *N*-methyl and the aromatic ring, the formation of 150^+, 117^+, and 91^+ can be rationalized as depicted in Scheme 2.

The mechanism suggested in Scheme 2 is based upon the assumption that the M − 1 ion is formed by the abstraction of a hydrogen atom from one of the methyl groups. However, it has been shown [13] that the M − 1 peak in the mass spectrum of *N*,*N*-dimethylbenzamide is due to the loss of a hydrogen from the phenyl group, thus questioning our assumption, but whereas the M − 1 ion from the *N*,*N*-dimethylbenzamide has not been observed to decompose further, the loss of ·SH from the M − 1 ions from IV and V as well as the formation of $C_7H_7^+$ ions are best interpreted by the mechanism above.

The mass spectrum of *N*,*N*-dimethylthiobenzamide (V, Fig. 5) contains peaks corresponding to some of the processes observed for the monomethyl analogue. It should be noted, however, that whereas the loss of ·SH took place from the molecular ion as well as from the M − 1 ion of IV, the dimethyl derivative primarily undergoes ·SH abstraction from the M − 1 ion. This difference can be taken as evidence for a thiolization of IV prior to the loss of ·SH. Due to the absence of a hydrogen bonded to nitrogen in V, this compound is unable to undergo enethiolization.

Walter *et al.*[8] have discussed the mass spectra of various thioformanilides. A dominating feature of the mass spectra of these compounds is the presence of abundant M − 1 peaks. These peaks are due to ions formed by the abstraction of an *ortho*-hydrogen from the phenyl group. In the mass spectrum (Fig. 6) of thioacetanilide (VI) an abundant M − 1 peak at *m/e* 150 is found, and this

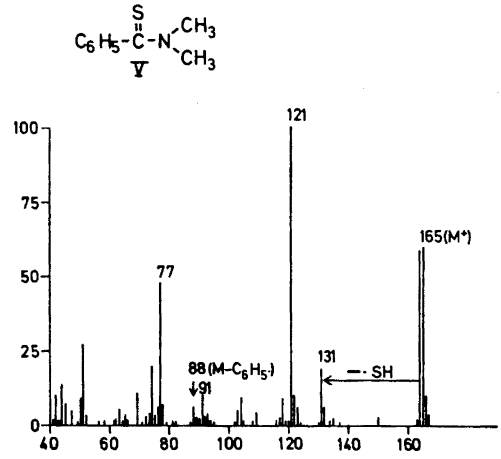
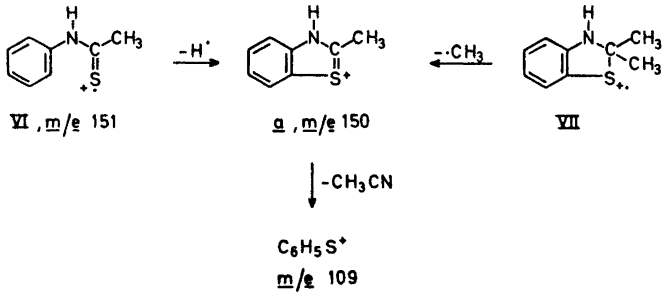


Fig. 5

peak is also prominent at low voltage. If it is assumed that an *o*-hydrogen is abstracted from the aromatic ring in connection with bond formation, the structure of the M − 1 ion can be depicted as *a* (Scheme 3). A metastable peak at *m/e* 79.2 indicates the loss of CH_3CN from *a*. In order to investigate the structure of the M − 1 ion further, the mass spectrum of 2,2-dimethyl-2,3-dihydrobenzthiazole (VII) was recorded, as the same 150^+ ion was expected to be formed by the loss of $\cdot CH_3$ from the molecular ion. The mass spectrum of VII displays only three prominent peaks corresponding to M, M − $\cdot CH_3$, and M − $\cdot CH_3$ − CH_3CN. The metastable peak at 79.2 ($150^+ \rightarrow 109^+$) mentioned above was also found in the mass spectrum of VII, supporting the assumed mechanism (Scheme 3).



Scheme 3.

Loss of acetonitrile not only takes place from the M − 1 ion, but also from the molecular ion, leading to ionized thiophenol (*m/e* 110). Loss of ·SH from the molecular ion is also observed. The abundant peak at *m/e* 93 corresponds to ionized aniline.

In the mass spectrum (Fig. 7) of *p*-methylthioacetanilide (VIII) the features of thioacetanilide (VI) are found. The presence of an abundant M − 2 doubly charged ion peak at *m/e* 81.5 (15 %) can be assigned to the formation of *b*.

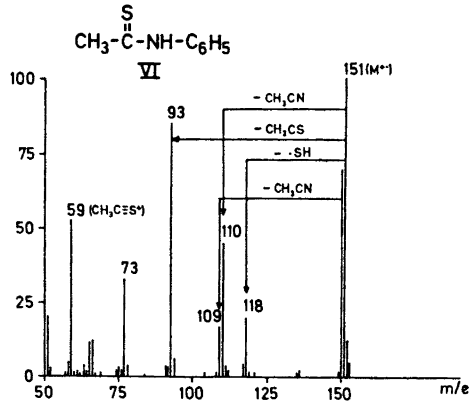
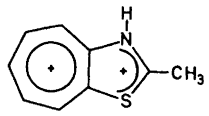


Fig. 6



b, m/e 81.5

As it was not possible to obtain a sample of *o*-thioacetotoluid completely free of the oxygen analogue, the mass spectrum is not reported here. As in the case of the *p*-isomer an abundant peak is observed at *m/e* 81.5, but whereas

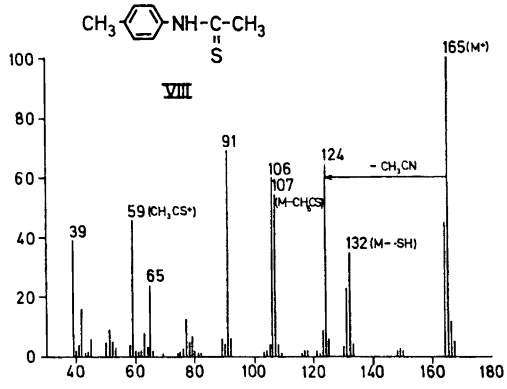


Fig. 7

the *p*-isomer eliminates a hydrogen atom from the molecular ion, this compound undergoes the loss of a methyl radical.

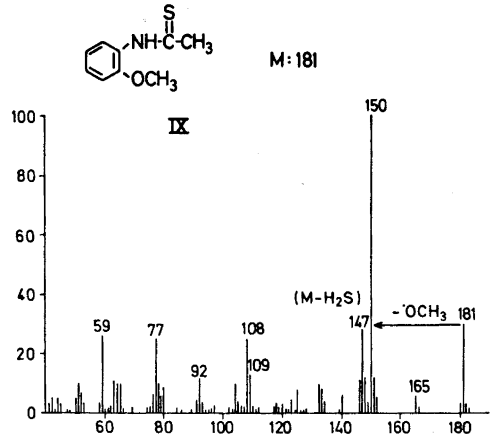


Fig. 8

Corresponding to this process *o*-methoxythioacetanilide (IX) undergoes the loss of a methoxy group leading to the formation of *a*, whereas the mass spectrum of the *p*-isomer (not reported here) only displays a minor M − 31 peak.

EXPERIMENTAL

The mass spectra were recorded with an AEI MS 902 doubly focussing mass spectrometer, using the direct inlet with a source temperature of 100 − 135°C.

All thioamides were either commercially or synthesized in known ways.[14]

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