Electron Impact Studies

CXXIV†—Negative Ion Mass Spectra of Organic Functional Groups. Thioacetanilides

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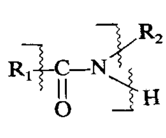
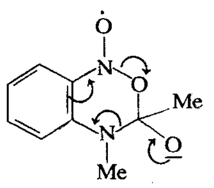
The thioacetanilide negative molecular ion (produced by secondary electron capture) is stable, but it fragments after collisional activation to yield $[C_6H_5NH]^-$ by cleavage α to the C═S grouping. The negative molecular ions of (substituted) *o*-nitrothioacetanilides undergo a series of extremely complex rearrangement reactions. For example, the molecular anion derived from *o*-nitro-*N*-methylthioacetanilide yields both acetate and thioacetate anions as major fragment ions.

INTRODUCTION

As part of our studies of the behaviour of negative molecular ions produced by secondary electron capture,[1] we have shown that fragmentation of a simple amide only occurs under conditions of collisional activation.[2] The basic cleavages of amides are shown in *a*. A number of unimolecular rearrangement reactions occur from negative molecular ions derived from *o*-nitroacetanilides;[3–5] such *ortho* effects are of common occurrence in spectra arising from the low energy negative molecular ions of suitably substituted aromatic compounds.[1] For example, the acetate negative ion constitutes the base peak in the spectrum of *o*-nitro-*N*-methylacetanilide (see *b*).[5]



a

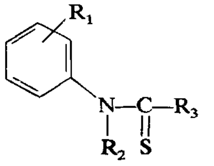


b

We expected that negative ions derived from thioamides would behave in a similar fashion to amides, particularly in respect of rearrangement reactions, since the negative ion spectra of sulphur compounds are often dominated by complex rearrangements.[6–8] This paper describes the behaviour of the thioamide group. As in past studies,[1] we used the nitrophenyl group both as the electron capture group, and also to permit the study of any *ortho* effects which may occur between the nitro group and the substituent under study.

RESULTS AND DISCUSSION

Compounds **1–11** were used for this study. The spectra of the unlabelled compounds are either listed in Table 1, or reproduced in Fig. 1.



Compound	R_1	R_2	R_3
1	H	H	Me
2	*o*-NO_2	H	Me
3	*o*-NO_2	D	Me
4	*m*-NO_2	H	Me
5	*m*-NO_2	D	Me
6	*p*-NO_2	H	Me
7	*p*-NO_2	D	Me
8	*o*-NO_2	Me	Me
9	*o*-NO_2	Me	CD_3
10	*p*-NO_2	Me	Me
11	*p*-NO_2	Me	CD_3

The basic fragmentations of the thioamide group

The spectrum (Table 1) of thioacetanilide (**1**) contains only a negative molecular ion and a smaller $[M-1]^-$ ion. Admission of nitrogen gas (3×10^{-5} Torr) into the first field free region (1st FFR) produces two gaussian peaks at *m*/*e* 149.0 and 56.1 due to the respective collision induced processes $[M]^{-\cdot}\rightarrow[M-H^\cdot]^-$ and $[M]^{-\cdot}\rightarrow[M-MeCS^\cdot]^-$. The spectra of *m*- and *p*-nitrothioacetanilide also show peaks due to $[M-H^\cdot]^-$ and $[M-MeCS^\cdot]^-$ ions (see Table 1), with appropriate decompositions in the field free regions being strongly collision induced. The corresponding fragmentations from the molecular anion of *p*-nitro-*N*-methylthioacetanilide are $[M]^{-\cdot}\rightarrow[M-Me^\cdot]^-$ and $[M]^{-\cdot}\rightarrow[M-MeCS^\cdot]^-$. The spectra of the *N*–D

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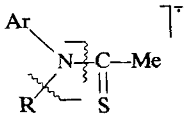
Table 1. Negative ion mass spectra of 1, 2, 4, 6 and 10[a]

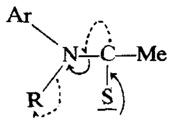
Compound	$[M]^{-\cdot}$	$[M-H^{\cdot}]^{-}$	$[M-Me^{\cdot}]^{-}$	$[M-HO^{\cdot}]^{-}$	$[M-NO^{\cdot}]^{-}$	$[M-HS^{\cdot}]^{-}$	$[M-HNO_2]^{-\cdot}$	$[M-SO]^{-\cdot}$	$[M-MeCS^{\cdot}]^{-}$	$[MeCOS]^{-}$	$[NO_2]^{-}$
1	100	20									
2	45	100		16		58		11		18	8
4	100	19		10	1		15		2		15
6	80	100		6	1		6		2		18
10	100		6		6				3		16

[a] All fragmentations shown are substantiated by the presence of peaks corresponding to the appropriate metastable ion (unimolecular process) or collision induced ion.

analogues **5** and **7** show $[M-D^{\cdot}]^{-}$ ions, while that of the D_3 derivative **11** exhibits an $[M-CH_3^{\cdot}]^{-}$ ion. Therefore, the two basic cleavages of the thioacetanilide system are those shown in *c*. Both are collision induced, and may be rationalized as proposed in *d* (R = H or Me) (compare amides, see *a*). Other fragmentations noted for **4**, **6** and **10** are characteristic of aryl nitro compounds and have been described previously.[1-5]



c



d

Rearrangement reactions of *o*-nitrothioacetanilides

The spectrum (Table 1) of *o*-nitrothioacetanilide (**2**) is dominated by rearrangement fragments. The two major processes are $[M]^{-\cdot} \rightarrow [M-HO^{\cdot}]^{-}$ and $[M]^{-\cdot} \rightarrow [M-HS^{\cdot}]^{-}$; these become $[M]^{-\cdot} \rightarrow [M-DO^{\cdot}]^{-}$ and $[M]^{-\cdot} \rightarrow [M-DS^{\cdot}]^{-}$ in the spectrum of **3**. The loss of $HO^{\cdot}$ is characteristic of a nitrobenzene containing an *o*-NH(C=X)- unit (X = O[4] or S). A possible rationale for this process from **2** involves hydrogen rearrangement in the negative molecular ion to form *e* (hydrogen migrations to nitro oxygens are relatively common in negative ions[9]), which would then eliminate an hydroxyl radical as shown. The loss of $HS^{\cdot}$ is not observed in the spectra of the corresponding *m*- and *p*-isomers, so the fragmentation mechanism is unlikely to involve simple 1,2-elimination through a 4-membered transition state. The negative molecular ion of *o*-nitro-*N*-methylthioacetanilide (**8**) rearranges to *f* (R = Me) (see below); a similar rearrangement of the *o*-nitrothioacetanilide negative molecular ion could yield *f* (R = H) which may lose $HS^{\cdot}$ by a similar mechanism to that proposed for loss of $HO^{\cdot}$ (cf. *e*). A peak due to the thioacetate negative ion is also observed in small abundance in the spectrum of **2**; this ion is produced by an oxygen rearrangement directly comparable with that shown in *b*. The mechanism of the final rearrangement, $[M]^{-\cdot} \rightarrow [M-SO]^{-\cdot}$, is not known.

If the NH hydrogen is replaced by a methyl group (as in **8**), a number of new rearrangement channels are noted, since fragmentation involving the NH is now blocked. Of the observed reactions (see Fig. 1), $[M]^{-\cdot} \rightarrow [MeCOS^{\cdot}]^{-}$ ($[M]^{-\cdot} \rightarrow [CD_3COS^{\cdot}]^{-}$ in the spectrum of **9**), and $[M]^{-\cdot} \rightarrow [M-MeCOS^{\cdot}]^{-}$ ($[M]^{-\cdot} \rightarrow [M-CD_3COS^{\cdot}]^{-}$ in the spectrum of **9**), are predictable (see e.g. *b*). The reactions $[M]^{-\cdot} \rightarrow [MeCO_2]^{-}$, $[M-NO^{\cdot}]^{-} \rightarrow [(M-NO^{\cdot})-CH_2CO^{\cdot}]^{-}$ and $[M]^{-\cdot} \rightarrow [NOS]^{-}$ are more complex, and were not expected. The first two of these reactions become $[M]^{-\cdot} \rightarrow [CD_3CO_2]^{-}$ and $[M-NO^{\cdot}]^{-} \rightarrow [(M-NO^{\cdot})-CD_2CO]^{-}$ in the spectrum of **9**. The precursor to these unusual rearrangement ions may be *f* (R = Me), since this ion can account for the three rearrangements just described. The formation of *f* from the negative molecular ion of **8** must involve at least three discrete cyclizations; any proposed mechanism would be speculative. The ion *f* may fragment to $[NOS]^{-}$, it may rearrange to yield the acetate negative ion (see *g* and cf. *b*), and it may lose $NO^{\cdot}$ to produce *h* which in turn may eliminate ketene.[cf.3]

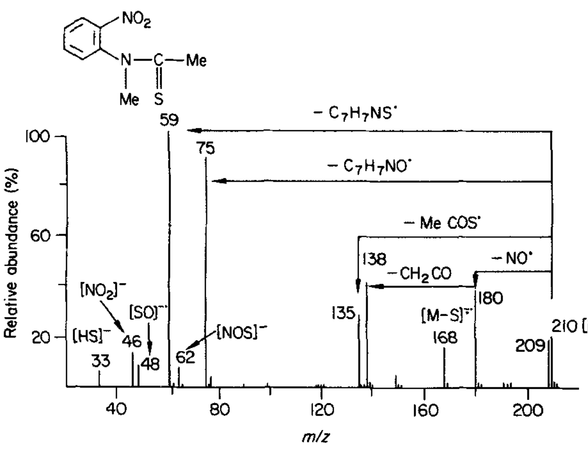
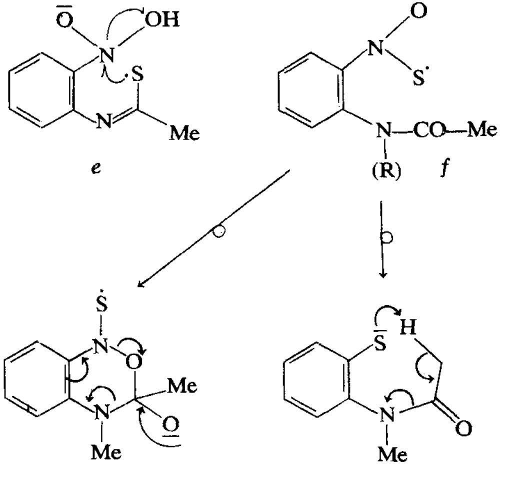


Figure 1



e *f* *g* *h*

The metastable peak for the process $[M]^{-\cdot} \rightarrow [M-NO^{\cdot}]^{-}$ from **8** is Gaussian with a kinetic energy release at half-height of 0.037 ± 0.005 eV. This should be contrasted with dish-shaped metastable peaks with large energy releases (0.2–0.8 eV at half-height) observed for the losses of $NO^{\cdot}$ from intact nitro groups.[10] Nitro groups are thought to eliminate $NO^{\cdot}$ by a concerted rearrangement through a 3-membered transition state.[10] The small energy release accompanying decomposition of the NOS group points to a stepwise rearrangement to the $\text{-S-}\dot{N}\text{-O}^{-}$ ion, which subsequently eliminates $NO^{\cdot}$.

The formation of *f* and its subsequent decompositions consitute the most complex series of rearrangements yet documented for negative ions.

EXPERIMENTAL

All spectra were measured with an Hitachi Perkin Elmer RMU 7D mass spectrometer modified as specified previously.[11] Spectra were routinely measured at 70 eV using a source pressure of 1×10^{-6} Torr, and an accelerating potential of 3.6 kV. Samples were introduced through an all-glass inlet system maintained at 100 °C. Collision activation spectra[12] were measured using a nitrogen pressure of 3×10^{-5} Torr in the 1st FFR. Elemental analyses were performed by NOVO Microanalytical Laboratory, Novo Industry A/S, Denmark.

All thioamides, with the exception of **8**, are known; viz. **1**[13] (**2**, **4** and **6**)[14] and **9**.[15] All thioamides were prepared in near quantitative yield (95–100%) by the following general method.[16]

A mixture of the appropriate precursor amide (0.01 mol) and *p*-methoxyphenylthionophosphin sulphide dimer (2.5 g, 0.006 mol) was heated under reflux in dry toluene for 4 h. Removal of the solvent followed by chromatography over silica gel 60 in light petroleum/diethyl ether (10–50% ether depending upon the particular system), yields the thioamide which was crystallized from isopropyl ether as yellow needles.

***o*-Nitro-*N*-methylthioacetanilide,** m.p. 64–66 °C, had the following analytical figures: C 51.2, H 4.85, N 13.25, S 15.1%. $C_9H_{10}N_2O_2S$ requires C 51.4, H 4.8, N 13.3, S 15.3%

The spectra of the D_1 derivatives **3**, **5** and **7** were obtained by admitting **2**, **4** and **6** directly into the source in the presence of D_2O.[17] Incorporations of 70–80% were obtained.

Compound **9** was prepared from the amide **8**.[18] Compound **8** (210 mg) was dissolved in C_6D_6 (2.5 cc) and added to aqueous NaOD (1 cc, 5%) containing *n*-Bu_4NHSO_4 (17 mg), and the mixture allowed to stir for 30 min. Compound **9** ($D_0 = 23$, $D_1 = 40$, $D_2 = 25$, $D_3 = 12\%$) was purified by sublimation.

Acknowledgements

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REFERENCES

1. J. H. Bowie and B. D. Williams, 'Negative Ion Mass Spectrometry of Organic, Organometallic and Coordination Compounds,' in *International Reviews of Science, Mass Spectrometry*, Physical Chemistry, Series Two, Vol. 5, ed. by A. Maccoll, pp. 89–127. Butterworths, London (1976) and references cited therein.
2. J. H. Bowie, *Aust. J. Chem.* **26**, 2719 (1973).
3. J. H. Bowie, *Org. Mass Spectrom.* **5**, 945 (1971).
4. J. H. Bowie, *Aust. J. Chem.* **24**, 989 (1971).
5. J. A. Benbow, J. C. Wilson and J. H. Bowie, *Int. J. Mass Spectrom. Ion Phys.* **26**, 173 (1978).
6. J. H. Bowie and A. C. Ho, *Aust. J. Chem.* **26**, 2009 (1973)
7. J. C. Wilson and J. H. Bowie, *Org. Mass Spectrom.* **10**, 836 (1975).
8. J. Rüllkotter and H. Budzikiewicz, *Org. Mass Spectrom.* **11**, 44 (1976).
9. B. A. Hale and J. H. Bowie, *Org. Mass Spectrom.* **11**, 1105 (1976).
10. J. H. Bowie, T. Blumenthal and P. Y. White, *Aust. J. Chem.* **31**, 573 (1978)
11. J. H. Bowie and S. G. Hart. *Int. J. Mass Spectrom. Ion Phys.* **13**, 319 (1974).
12. J. H. Bowie, *J. Am. Chem. Soc.* **95**, 5795 (1973).
13. A. W. Hofmann, *Chem. Ber.* **11**, 339 (1978).
14. G. Hopkins and L. Hurter, *J. Chem. Soc.* 638 (1942).
15. J. Voss and W. Walter, *Ann.* **743**, 177 (1971).
16. S. Scheibye, B. S. Pedersen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.* in press.
17. J. S. Shannon, *Aust. J. Chem.* **15**, 265 (1962).
18. C. M. Starks, *J. Am. Chem. Soc.* **93**, 189 (1971).

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