

Mass Spectra of 1-Carboxyethyl-3-Aryl-2-Thioureas

B. DASH and P. K. MAHAPATRA

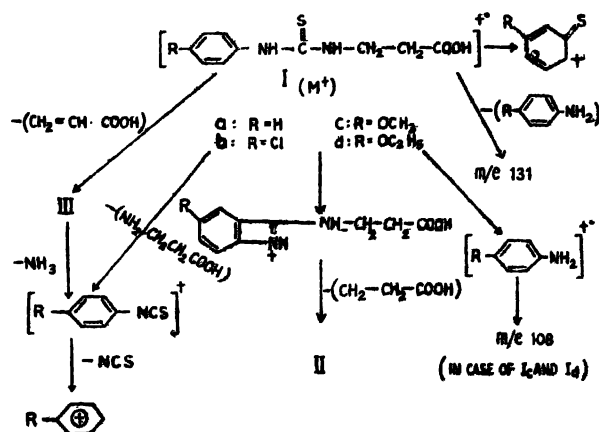
Department of Chemistry, Utkal University,
Bhubaneswar-751 004

Manuscript received 13 December 1982, revised 1 October 1983,
accepted 3 December 1983

THE synthesis and biological activities of some 1-carboxyethyl-3-aryl-2-thioureas containing thiourea and amino acid moiety and their metal complexes have already been reported¹. Since mass spectrometry provides a valuable tool for structural analysis, it seemed of interest to examine the electron impact induced fragmentation of the above thioureas. The mass spectra were recorded in a Varian MAT SM 1-BH spectrophotometer in the University of Wurtzberg and at C.D.R.I., Lucknow at a voltage of 70 eV.

Although a few papers dealing with mass spectrometry of ureas², thioureas³ and amidino thioureas⁴ have been published: it appears that no report has been made to date on carboxyethyl thioureas (I). In this type of compounds it may be expected that the initial charge is localised preferentially on either nitrogen, sulphur or an aromatic ring.

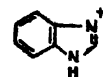
Mass spectra of 1-carboxyethyl-3-aryl-2-thiourea: The mass spectra of four thioureas (I, R=H, Cl, OCH₃, OC₂H₅) have been investigated. All the compounds yielded easily recognisable molecular ions with characteristic isotopic contribution and weak (M-1) peaks. The principal fragmentation peaks are given in Scheme 1.



Scheme 1

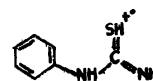
All the carboxyethyl thioureas contain the peaks corresponding to the loss of 33 mass units from the molecular ion (M-SH)⁺. Earlier workers^{5a} by deuterium labelling postulated the formation of a 4-membered (M-SH)⁺ ion in the mass spectra of aryl thioureas, thus indicating that the 'SH' hydrogen may originate from one of the aryl orthohydrogens. This

fragmentation root was supported by corresponding metastable peaks. Loss of CH₂-CH₂-COOH from (M-SH)⁺ ion and subsequent rearrangement resulted in a benzimidazole ion (II) in all the four thioureas. This may occur with or without hydrogen transfer.



II

An ion of mass corresponding to (M-72) units (III) in the spectra of some thioureas can be envisaged as occurring by way of McLafferty rearrangement, although in some instances it was of low abundance.



III

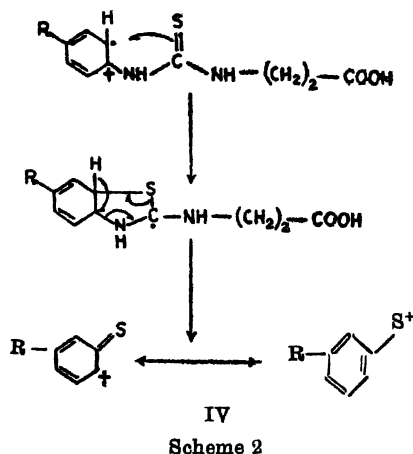
Each of the four carboxyethyl thioureas contains an abundant peak due to the elimination of a β -alanine unit. These peaks are either the base peak or next to that and may be represented as (R-C₆H₄-NCS)⁺, the formation of which may be explained in terms of McLafferty rearrangement. A metastable peak at 81.5 in **Ia** verified the genesis of this ion from one step decomposition of the molecular ion. The subsequent decomposition of this ion by the expulsion of -NCS afforded the phenyl or substituted phenyl ion. Similar elimination of NCS from (C₆H₅NCS)⁺ has also been observed by Djerassi *et al*⁶.

A peak of moderate intensity at m/e 136 was observed in the case of **Ia** which may arise because of the formation of (C₆H₅-NH=C=S)⁺ ion. The corresponding peaks were also observed in other thioureas.

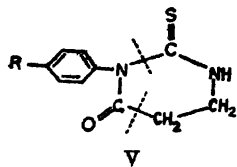
Another peak at m/e 78 was observed in the case of **Ia** which was formed by the elimination of HOOC-(CH₂)₂-NH-CNS from the molecular ion. Peaks corresponding to this were also observed in the other thioureas. Similar peak has also been observed by Grehn⁶.

A fragment ion at m/e 93 in the spectrum of **Ia** corresponds to ionised (C₆H₅NH₂)⁺. A metastable ion at mass 38.5 affords evidence of the fact that this ion is formed by a single step decomposition from the molecular ion. The peaks corresponding to m/e 93 also occurred in the spectra of other carboxyethyl thioureas. These ions decomposed further according to the process for fragmentation of substituted aniline⁷. Thus, further fragmentation of *p*-OCH₃ and *p*-OC₂H₅ aniline ion gave an ion at m/e 108 by the elimination of CH₃ and C₂H₅, respectively. A peak at m/e 109 in the case of the mass spectra of **Ia** and at the corresponding mass units in case of other thioureas are observed with moderate intensity.

This may be attributed to the formation of $(R-C_6H_4S)^+$ (IV), a possible mechanistic rationalisation for the formation of which is given below^{8a} (Scheme 2).



Other prominent peaks observed are due to the loss of OH, H₂O and COOH as is evidenced in the case of acids. Peaks at *m/e* 132 and 131 are observed in all the thioureas by loss of ArNH and ArNH₂, respectively from the molecular ions. Peaks of moderate intensity corresponding to the ion $(R-C_6H_4-N-C=O)^+$ were observed in the case of all the thioureas. The formation of this ion may be rationalised by the breaking of 2-3 and 4-5 bonds of a 3-substituted-2-thio-dihydrouracil (V) which might have been formed by the loss of water molecule from the parent ion.



References

1. B. DASH and S. K. MAHAPATRA, *J. Indian Chem. Soc.*, 1973, 50, 738; *J. Inst. Chem.*, 1977, 49, 54.
2. a. H. BUDZIKIEWICZ, C. DJERASSI and D. H. WILLIAMS, "Mass Spectrometry of Organic Compounds", Holden Day, Inc., Francisco, 1967, p. 503.
- b. M. A. BALDWIN, A. KIRKIEN-KONASIEWICZ, A. G. LOUDON, A. MACCOLL and D. SMITH, *Chem. Commun.*, 1966, 574.
3. a. R. H. SHAPIRO, J. W. SERRUM and A. M. DUFFELD, *J. Org. Chem.*, 1968, 33, 243.
- b. M. A. BALDWIN, *Org. Mass Spectrom.*, 1970, 4, 81.
4. T. URDA, A. TAKADA, K. TAKAHASHI and F. URDA, *Chem. Pharm. Bull.*, 1971, 19, 1990.
5. A. KJAER, M. OHASHI, J. M. WILSON and C. DJERASSI, *Acta Chem. Scand.*, 1963, 17, 2143.
6. L. GREEN, *Org. Mass Spectrom.*, 1977, 12, 267.
7. G. SPITELLER and M. SPITELLER-FRIEDMANN, *Monatsh.*, 1962, 93, 1395.

Effect of Substituents on Chromatographic Behaviour of Imines

MANGAT RAI*, BALJIT, RENU, B. S. DHIR

and

P. S. KALSI

Department of Chemistry, Punjab Agricultural University, Ludhiana-141 004

Manuscript received 4 January 1983, revised 26 September 1983, accepted 27 February 1984

MOST organic compounds have been studied by thin layer chromatography¹. However, no systematic study²⁻⁴ on the tlc of the imines⁵ has been made so far. This communication describes the tlc of 21 imines using methanol-H₂SO₄ (95 : 5 v/v) as spraying reagent and the effect of substituents on the R_f values of the imines. The results of this study are at variance with those reported earlier².

Experimental

Benzal anilines, *p*-chlorobenzal anilines and *p*-methoxybenzal anilines were prepared by condensing aniline and substituted anilines with benzaldehyde, *p*-chlorobenzaldehyde and anisaldehyde, respectively.

Silica gel G (Polypharm., Bombay, 100 g) and water (200 ml) was stirred thoroughly to give a fine slurry. The mixture was then coated on glass plates (20 × 5 cm) to a thickness of about 0.10 cm. The plates were air dried (15 min) and activated for 4 hr at 120° in an oven. Sample solutions were prepared in methanol and applied with fine capillaries on the activated plates. The plates were developed in glass chambers with ground in lids by ascending technique for 20 min. The developed plates were air dried, sprayed with methanol-sulphuric acid mixture (95 : 5 v/v) and heated in an oven till the spots were clearly discernible.

Results and Discussion

The highest R_f values were obtained from benzene-methanol (1 : 1), but the resolution was poor. Benzene showed a high resolving capability, but the best results were obtained in benzene-ethylacetate (95 : 5) for most of the imines. R_f values of the imines were found to be independent of the plate size.

The effect of substitution in C-phenyl ring/N-phenyl ring on the R_f values was studied by comparing the values of substituted imine with those of imine of the unsubstituted benzaldehyde/aniline. It was observed that the presence of electron donor groups (CH₃, OCH₃, OC₂H₅, etc.) in the N-phenyl ring decreased the R_f values whereas electron withdrawing substituents (Cl, Br, NO₂) increased the values. These results are at variance with the earlier reported results². Regarding substitution in C-phenyl ring, both Cl and OCH₃ group in *p*-position showed an increase in the R_f values (Table 1).