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Note

Thin-layer chromatography of isothiocyanates and thioureas

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Isothiocyanates have been separated chromatographically only as their derivatives, such as thioureas¹ and thiosemicarbazides². An attempt by Wagner *et al.*¹ to separate them in their natural form did not meet with success.

A method has now been developed for the separation of a mixture of isothiocyanates on silica gel plates using *n*-hexane-cyclohexane (10:1) or *n*-hexane-benzene (10:1) as the solvent system.

Chloroform-ethyl acetate (10:1) is used to separate thioureas. Further, the separation of isothiocyanates and their corresponding thioureas is carried out using the same solvent system.

EXPERIMENTAL

Glass plates (20 × 20 cm) were coated with an aqueous slurry of silica gel (National Chemical Laboratory (NCL), Poona, India) using a Desaga spreader and were dried by heating in an oven at 105° for 30min.

Standard solution of isothiocyanates and thioureas

Phenyl isothiocyanate (0.005%, w/v), allyl isothiocyanate (0.5%, w/v), ethyl isothiocyanate (5.0%, w/v) and methyl isothiocyanate (5.0%, w/v) were prepared in chloroform. An ethanolic solution of thiourea (0.1%, w/v) was employed in each instance.

Spotting, development and detection

Isothiocyanates. A 5- μ l volume of isothiocyanate solution was a suitable sample size and *n*-hexane-cyclohexane (10:1) or *n*-hexane-benzene (10:1) was the most satisfactory solvent for the separation. After evaporation of the solvent, the plates were exposed to ammonia vapour for 20 min. They were then heated at 60-70° for 15 min, cooled to room temperature and sprayed with an ethanolic solution of 2,3-dichloro-1,4-naphthoquinone (0.026%, w/v). They were again exposed to ammonia vapour until pink spots were visible (about 5 min). The R_F values obtained are recorded in Table I.

Thioureas. A 1.0- μ l volume of thiourea solution was a suitable sample size and chloroform-ethyl acetate (10:1) was the most satisfactory solvent for the sepa-

TABLE I

 R_F VALUES OF ISOTHIOCYANATES

Each value is the average of five results.

<i>Isothiocyanate</i>	<i>Solvent system</i>	
	<i>n-Hexane-cyclohexane</i>	<i>n-Hexane-benzene</i>
Phenyl isothiocyanate	0.61	0.71
Ethyl isothiocyanate	0.12	0.23
Allyl isothiocyanate	0.33	0.43
Methyl isothiocyanate	0.35	0.45

TABLE II

 R_F VALUES OF THIOUREAS

Each value is the average of five results.

<i>Thiourea</i>	R_F value
Phenylthiourea	0.34
Allylthiourea	0.25
Ethylthiourea	0.15
Methylthiourea	0.05

TABLE III

 R_F VALUES OF ISOTHIOCYANATES AND THE CORRESPONDING THIOUREAS

Each value is the average of five results.

<i>Compound</i>	R_F value
Phenyl isothiocyanate	0.81
Phenylthiourea	0.34
Ethyl isothiocyanate	0.83
Ethylthiourea	0.15
Allyl isothiocyanate	0.84
Allylthiourea	0.25

ration. Detection was carried out as described above. The R_F values are recorded in Table II.

Isothiocyanate-thiourea mixtures. Volumes of 5 μ l of isothiocyanate solution and 1 μ l of the corresponding thiourea solution were co-spotted. The chromatograms were developed using chloroform-ethyl acetate (10:1) and were then treated as described above. Detection was carried out by spraying with an ethanolic solution of 2,3-dichloro-1,4-naphthoquinone (0.026%, w/v). The R_F values are given in Table III.

RESULTS

Recently, a colour reaction between isothiocyanates and 2,3-dichloro-1,4-naphthoquinone in the presence of ammonia has been described³. Isothiocyanates are known to react with ammonia to give corresponding thioureas:



The thiourea thus formed reacts with 2,3-dichloro-1,4-naphthoquinone to give a pink-coloured product on basifying the reaction mixture with ammonia. Detection of isothiocyanates and thioureas is based on the above reaction.

Phenyl, allyl, ethyl and methyl isothiocyanate are detected in 0.2, 25, 250 and 250 μg amounts, respectively, while their thioureas can be detected in 1- μg amounts. The R_F values obtained for isothiocyanates and thioureas are reported in Tables I and II.

It is evident from Table III that in each instance the R_F value of an isothiocyanate is considerably higher than that of the corresponding thiourea, and their separation can therefore be easily achieved.

The procedure may be useful for kinetic studies of the reaction between isothiocyanates and ammonia.

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REFERENCES

- 1 H. Wagner, L. Horhammer and H. Nufer, *Arzneim.-Forsch.*, 15 (1965) 453.
- 2 S. Fisel, F. Modreanu and A. Carpov, *Acad. Repub. Pop. Rom., Fil. Iasi, Stud. Cercet. Stiint., Chim.*, 7 (1956) 19.
- 3 M. B. Devani, C. J. Shishoo and M. G. Shah, *Analyst (London)*, 98 (1973) 759.