

CHROM. 5194

Identification of organic compounds**LXXV*. Paper and thin-layer chromatography of simple s-triazine derivatives**

During the investigation of the hydrolysis of technologically important s-triazine derivatives it was necessary to carry out analyses of the reaction mixtures and to identify the hydrolysis products, especially the hydroxy and amino derivatives of s-triazine. The use of some of the usual chromatographic techniques seemed to be hopeful for this purpose. A review on the chromatography of s-triazine derivatives has been published recently¹. Most of the work involved in this review as well as other contributions in the chemical literature deal with compounds used as herbicides²⁻⁵ or melamine resins⁶⁻¹⁶. Our interest was especially directed to cyanuric acid and melamine which have been dealt with by only a few authors¹⁶⁻²².

From this work and our preliminary experiments it was evident that no troubles should be expected in finding a suitable solvent system. But a critical evaluation of the detection reagents that had been recommended previously seemed to be necessary. The detection reagents were expected to be of great importance in the evaluation of the chromatograms of the complex hydrolysis products. The reagents recommended by previous authors have been summarised in Table I.

It is evident that there is a series of colour reactions available for the detection of melamine on chromatograms whereas cyanuric acid is only detected with some difficulty. Thus, *e.g.* melamine, ammeline and ammelide have been detected easily using reagent V on chromatograms of the reaction mixture after the acid hydrolysis of melamine resins⁸, but the identification of cyanuric acid is only achieved after

TABLE I

METHODS OF DETECTION OF S-TRIAZINE DERIVATIVES^a

No.	Reagent	Cyanuric acid	Melamine	References
I	Ehrlich's reagent		+	7, 11, 13
II	Ammoniacal AgNO ₃	+	+	7, 10, 17
III	Dichloroquinonechloroimine	-	+	7, 10
IV	Chlorine + <i>o</i> -tolidine		+	6
V	Potassium ferricyanide + sodium nitroprusside + NaOH		+	7, 8
VI	Picric acid		+	9
VII	Iodine-potassium iodide		+	11
VIII	Formaldehyde + ammonium nitrate + sodium acetate + Ponceau 6R		+	12
IX	Formaldehyde + argent nitrate		+	14
X	Antimony(III) chloride	-	+	10
XI	Brucine		+	10
XII	<i>o</i> -Tolidine		+	10
XIII	Ninhydrin	-	+	10
XIV	8-Hydroxyquinoline + fluorescein	-	+	10
XV	Formaldehyde + Schiff's reagent	-	+	19
XVI	Mercury acetate + diphenylcarbazone	+		20
XVII	Ammoniacal copper acetate	+		16

^a + Positive reaction; - negative reaction.

* Part LXXIV: *J. Chromatogr.*, 54 (1971) 436.

total hydrolysis in the classical manner by isolation and conversion into a violet precipitate with an ammoniacal solution of copper hydroxide.

During our experiments the solvent system 1-propanol-ammonia (2:1) proved to be useful for paper chromatography. Both this solvent system and 1-butanol saturated with ammonia were found to be suitable for the thin-layer chromatographic separation. A good resolution of the hydrolysis products and the starting compounds was achieved in these systems and the spots of cyanuric acid and other hydroxy and amino derivatives of *s*-triazine were well-formed and round.

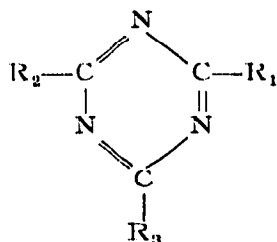
The combination of the following two methods of detection proved to be the most convenient: spraying with mercury acetate and diphenylcarbazone to detect the hydroxy and amino derivatives and spraying with formaldehyde and Schiff's reagent to detect the amino derivatives.

Experimental

Paper chromatography. Whatman No. 3MM paper and the solvent system 1-propanol-ammonia (2:1) were used throughout all the experiments. 5 μ l of 5%

TABLE II

R_F VALUES OF *S*-TRIAZINE DERIVATIVES



Solvent systems: S_1 = 1-propanol-ammonia (2:1); S_2 = 1-butanol saturated with 25% ammonia; Detection methods: D_1 = mercury acetate + diphenylcarbazone; D_2 = silver nitrate + potassium hydroxide; D_3 = formaldehyde + Schiff's reagent.

Compound			PC	TLC		Detection		
R_1	R_2	R_3		S_1	S_2	D_1	D_2	D_3
OH	OH	OH	0.25	0.42	0.23	blue violet	white	—
NH ₂	NH ₂	NH ₂	0.27	0.39	0.31	blue	white	carmine
Phenyl	NH ₂	NH ₂	0.77	0.88	0.87	blue	white	blue violet
<i>p</i> -Tolyl	NH ₂	NH ₂	0.80	0.88	0.87	blue	white	blue violet
<i>o</i> -Chlorophenyl	NH ₂	NH ₂	0.79	0.88	0.87	blue	white	blue violet
<i>p</i> -Cyanophenyl	NH ₂	NH ₂	streak	—	—	blue	white	blue violet
Phenyl	OH	OH	0.62	0.80	0.60	blue violet	white	—
<i>p</i> -Tolyl	OH	OH	0.63	0.83	0.63	blue violet	white	—
<i>m</i> -Tolyl	OH	OH	0.66	0.83	0.63	blue violet	white	—
<i>p</i> -Cyanophenyl	OH	OH	0.66	0.84	0.63	blue violet	white	—
<i>p</i> -Hydroxyphenyl	OH	OH	0.57	—	—	blue violet	white	—
<i>p</i> -Methoxyphenyl	OH	OH	0.82	0.73	0.55	blue violet	white	—
Bis(hydroxyethyl)-amino	NH ₂	NH ₂	0.38	—	—	blue	white	blue violet
—NH·C ₆ H ₅	—NH·C ₆ H ₅	—NH·C ₆ H ₅	0.94	—	0.97	blue	—	blue violet
OCH ₃	OH	OH	0.43	—	—	blue violet	white	—
OCH ₃	OCH ₃	OH	0.54	—	—	blue violet	white	—
OCH ₃	OCH ₃	OCH ₃	0.77	—	—	blue violet	white	—
Phenylene-bis-(diamino- <i>s</i> -triazine)			streak	—	—	blue	white	blue violet

solutions of s-triazine derivatives in dimethylsulphoxide were applied on the starting line and the development was carried out overnight.

Thin-layer chromatography. Thin layers were prepared in the usual manner using Cellulosepulver No. 142 dg (Schleicher and Schüll), the thickness of the layer being 0.5 mm. The systems 1-propanol-ammonia (2:1) (S_1) or 1-butanol saturated with ammonia (S_2) were both used as mobile phases.

Detection method D_1 . The chromatogram was sprayed with an ethanolic solution of mercury acetate (0.25 g of mercury acetate dissolved in 100 ml of 96% ethanol with 2 drops of acetic acid added) and after drying was sprayed with a 0.05% alcoholic solution of diphenylcarbazone. Then the chromatogram was heated in a drying oven at 125° for 3–5 min until the blue violet background had disappeared.

Detection method D_2 . The chromatogram was drawn through a freshly prepared solution of silver nitrate in acetone (100 ml of acetone mixed with 1 ml of a 5% aqueous solution of $AgNO_3$) and after drying it was sprayed with a (1:1) mixture of a 5% aqueous KOH solution and ethanol.

Detection method D_3 . The chromatogram was sprayed with a diluted formaldehyde solution (2 ml of formaldehyde diluted with 48 ml of water) and dried at 120–140°. Then the Schiff's reagent (0.5 g fuchsin dissolved in 350 ml of water and 25 ml of 1 N HCl to which 2.3 g of sodium metabisulphite was then added and the solution diluted to 500 ml with water) was applied.

Using detection method D_1 as little as 0.01–0.025 μ g of cyanuric acid were still detectable. The results of our study are summarised in Table II.

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