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THE SEPARATION OF CHLORINATED DERIVATIVES OF HYDROQUINONE USING THIN-LAYER AND PAPER CHROMATOGRAPHY

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SUMMARY

Thin-layer and paper chromatographic procedures are described for the separation and identification of six chlorinated derivatives of hydroquinone. Adsorption thin-layer chromatography (silica gel) or reversed-phase paper chromatography (olive oil—stationary phase and diluted acetic acid—mobile phase) did not enable satisfactory separation of dichloro-derivatives. These compounds have been clearly separated on kieselguhr thin layers and paper impregnated with formamide using three solvent systems.

INTRODUCTION

In a study of the preparation of chlorinated derivatives of *p*-benzoquinone by oxidation of chlorinated hydroquinones¹, it was found necessary to develop a method for the chromatographic separation and qualitative detection of chlorinated derivatives of hydroquinone.

As in our previous communication², the aim of our investigation was to find a simple procedure for the separation of 2,6-dichloro-, 2,3,5-trichloro- and 2,3,5,6-tetrachloro-derivatives.

EXPERIMENTAL

Preparation of pure compounds

The methods of preparation of the individual compounds and their melting points (after recrystallization) are given in Table I. A commercial sample of hydroquinone was recrystallized from benzene (m.p. 170.3°). The reports of some authors³⁻⁶ are conflicting in several respects, especially with regard to the ease with which a pure halogenated hydroquinone may be isolated. For instance, as opposed to the report of PERATONER AND GENCO⁴, we were not able to isolate pure 2,3-dichlorohydroquinone from the reaction mixture (2-chlorohydroquinone was present as a by-product). For our purposes this compound was obtained using preparative TLC. 2% solutions of the compounds in acetone were applied.

TABLE I
THE CHLORINATED DERIVATIVES OF HYDROQUINONE

Compound	Melting point ^a (°C)	Reference
2-Chlorohydroquinone	104.0	3
2,3-Dichlorohydroquinone	144.5	4
2,5-Dichlorohydroquinone	170.0	5
2,6-Dichlorohydroquinone	162.5	6
2,3,5-Trichlorohydroquinone	136.5	7
2,3,5,6-Tetrachlorohydroquinone	234.0	b

^a The melting points were determined using Kofler's microscope.

^b This compound was prepared by chlorination of hydroquinone in glacial acetic acid and was obtained together with chloranil as a by-product. The pure substance was obtained by recrystallization of reaction mixture from water and ethanol.

Mobile phases

All solvents (analytical grade) were distilled and used without further purification. All developing solutions were mixed on v/v basis immediately before being put into the developing chamber. The following solvent systems were used: S₁ = benzene-ethyl acetate (5:1); S₂ = chloroform-ethyl acetate (2:1); S₃ = chloroform-acetone (5:1); S₄ = water-acetic acid (2:1); S₅ = chloroform-acetone (6:1).

Stationary phases

Solutions of formamide (Carlo Erba) in ethanol and olive oil in benzene were used for impregnation. I₁ = 10% formamide in ethanol; I₂ = 20% formamide in ethanol; I₃ = 10% olive oil in benzene.

Preparative thin-layer chromatography

Plates with layers (Silica Gel DF 5 with a UV indicator, Camag) 1 mm thick were prepared in the usual way (heating at 120°, 24 h). A Camag chromatocarger was used to apply the samples in the form of bands. Solvent system S₅ was used for the separations and the bands were located under UV light (254 nm).

Thin-layer chromatography

Kieselguhr layers. A slurry was obtained by adding 50 ml of distilled water to 25 g of Kieselguhr G (Merck). Plates, 20 × 20 cm, with thin layers (0.3 mm) were prepared using a Camag applicator. The plates were dried for 1 h at room temperature and then heated for 1 h at 120° in an oven. The plates were cooled and stored in a desiccator for at least 24 h before use. The impregnation was made in a chromatography chamber by allowing an impregnation solution to ascend the plate by capillary action. The solvents were then evaporated into the air from the layer at room temperature.

Silica gel layers. 15 × 15 cm reflex silica gel foils Silufol[®] UV 254 (Kavalier n.p.) with a UV indicator were used.

Chromatographic procedure. The solutions of pure substances or their mixture were applied on the starting line (1.5 cm from the lower edge of the plate). After drying the spots, the plates were placed in developing chambers saturated with

solvents and developed by the ascending method, until the solvent front had travelled 15 cm beyond the original spots. The precoated silica gel foils were developed to a height of 10 cm. All experiments were carried out at $21 \pm 1^\circ$.

Paper chromatography

Chromatography was carried out on Whatman No. 1 paper. The paper was impregnated by passing it through a solution of the stationary phase. The time for

TABLE II

R_F VALUES FOR THE THIN-LAYER CHROMATOGRAPHIC SEPARATION OF THE CHLORINATED DERIVATIVES OF HYDROQUINONE

KG = kieselguhr; SG = silica gel.

Compound	KG ^a /S ₁ I ₁	KG/S ₂ I ₂	KG/S ₃ I ₂	SG/S ₆
Hydroquinone	0.12	0.12	0.11	0.15
2-Chlorohydroquinone	0.34	0.26	0.26	0.35
2,3-Dichlorohydroquinone	0.52	0.40	0.38	0.56
2,5-Dichlorohydroquinone	0.58	0.45	0.43	0.57
2,6-Dichlorohydroquinone	0.64	0.50	0.48	0.59
2,3,5-Trichlorohydroquinone	0.76	0.63	0.62	0.70
2,3,5,6-Tetrachlorohydroquinone	0.83	0.72	0.70	0.83

^a Dried for 15 min after impregnation in all other cases dried for 20 min.

drying the paper after impregnation and for the applications of the hydroquinones to the start was so arranged that the chromatogram was placed in the chromatography chamber, previously saturated with vapours of the solvents to be used, in the 15th or 20th min after starting the impregnation. After the solvent front had travelled 25–27 cm from the starting line, the chromatograms were thoroughly air dried at room temperature.

Detection

Satisfactory colour development (Table IV) was achieved within 30 sec after completing the spraying with a solution of ammonia (or an aliphatic amine) in water (D₁). The spots on the silica gel layers were visualised using D₁ and UV light (D₂). For detection of the spots on kieselguhr layers and paper chromatograms the

TABLE III

R_F VALUES FOR THE PAPER CHROMATOGRAPHIC SEPARATION OF THE CHLORINATED DERIVATIVES OF HYDROQUINONE

Compound	S ₂ I ₂	S ₃ I ₂	S ₄ I ₃
Hydroquinone	0.15	0.14	0.77
2-Chlorohydroquinone	0.34	0.29	0.71
2,3-Dichlorohydroquinone	0.46	0.43	0.60
2,5-Dichlorohydroquinone	0.52	0.48	0.62
2,6-Dichlorohydroquinone	0.57	0.53	0.64
2,3,5-Trichlorohydroquinone	0.66	0.63	0.48
2,3,5,6-Tetrachlorohydroquinone	0.72	0.70	0.26

following detection method (D_3) was used. After treatment of the plate with D_1 , the layer was dried, a 0.5% solution of fluorescein in ethanol was applied and the spots were finally located under UV light (350 nm). The detection limits of all the compounds (under experimental conditions) are given in Table IV. Detection methods used were: $D_1 = 25\%$ ammonia; $D_2 =$ UV light (254 nm); $D_3 = D_1 + 0.5\%$ solution of fluorescein in ethanol + UV light (350 nm).

RESULTS AND DISCUSSION

All separations were carried out, using the various solvents (S) and impregnation solutions (I) given on p. 378. The R_F values of chlorinated derivatives of hydroquinone in the systems used are given in Tables II and III.

Solvents S_1 , S_2 and S_3 were found to be the most satisfactory developing systems both for the identification and separation of the chlorinated derivatives of hydro-

TABLE IV

DETECTION LIMITS ($\times 10^{-6}$ g) AND COLOURS OF CHLORINATED DERIVATIVES OF HYDROQUINONE (AFTER DETECTION)

P = paper; SG = silica gel; KG = kieselguhr.

Compound	SG	KG ^a	P	Colours on SG and P
Hydroquinone	1.0	2.0	1.5	dark brown
2-Chlorohydroquinone	1.0	2.0	1.5	dark brown
2,3-Dichlorohydroquinone	1.0	2.0	1.5	red brown
2,5-Dichlorohydroquinone	1.0	2.0	1.5	red brown
2,6-Dichlorohydroquinone	1.0	2.0	1.5	red brown
2,3,5-Trichlorohydroquinone	2.0	5.0	2.0	light brown
2,3,5,6-Tetrachlorohydroquinone	2.0	5.0	2.0	light green

^a Quenching of spots (D_3).

quinone on kieselguhr layers and papers impregnated with formamide as a stationary phase. No solvent system was found in the present study which yielded a good separation of the dichloro-derivatives of hydroquinone on silica gel (or kieselguhr impregnated with olive oil). When the three systems mentioned above were used, 2,3-dichloro-, 2,5-dichloro- and 2,6-dichlorohydroquinones were clearly separated.

Because of its symmetry, substitution of hydrogen by chlorine at any site in the hydroquinone molecule should have the same effect on the R_M value. It follows from graphical correlation (separation on kieselguhr thin layers and paper impregnated with formamide) that the dependence between R_M or R_F values and the number of Cl atoms in the hydroquinone molecule is linear with the exception of 2,3,5,6-tetrachlorohydroquinone, whose R_M or R_F value lies outside the linear dependence. We hope to explain this phenomenon in a later paper.

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