CHROM. 5034

Chromatographic studies of some halogenated quinones

I. Thin-layer chromatography of some chlorinated derivatives of *p*-benzoquinone

Although a number of papers deal with the chromatographic behaviour of substituted quinones, with the exception of chloranil[1] there is no report in the literature with regard to TLC of chlorinated *p*-benzoquinones. Two papers[2,3] have appeared on the separation and identification of some chlorinated derivatives of *p*-benzoquinone by paper chromatography. As can be concluded from the results of these authors, the R_F values of 2,6-dichloro-1,4-benzoquinone and 2,3,5-trichloro-1,4-benzoquinone are not very different, and therefore the methods used for separation of these compounds are not convenient.

The aim of our investigation was to find the most satisfactory developing system for separation of 2,6-dichloro-1,4-benzoquinone, 2,3,5-trichloro-1,4-benzoquinone and their mixtures with chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone).

Experimental

Preparation of pure compounds. All chlorinated derivatives of *p*-benzoquinone were prepared by methods described in the literature (Table I). All compounds were purified by several crystallizations. Melting points of the pure compounds obtained are listed in the same table. A commercial sample of *p*-benzoquinone was also recrystallized. The samples of chlorinated *p*-benzoquinones were dissolved in anhydrous benzene. *p*-Benzoquinone was dissolved in abs. ethanol. 1 % solutions were spotted.

TABLE I

SOME CHLORINATED DERIVATIVES OF *p*-BENZOQUINONE

Compound	*Melting point*[a] (°*C*)	*Reference*
2-Chloro-1,4-benzoquinone	57.0	4
2,3-Dichloro-1,4-benzoquinone	98.0	5
2,5-Dichloro-1,4-benzoquinone	159.0	6
2,6-Dichloro-1,4-benzoquinone	119.0	7
2,3,5-Trichloro-1,4-benzoquinone	169.5	8
2,3,5,6-Tetrachloro-1,4-benzoquinone(chloranil)	289.5	9

[a] = The melting points are corrected.

Mobile phases. All solvents were redistilled before use. All mixtures were allowed to reach the temperature at which the chromatograms were to be eluted. All solvents used were reagent grade.

Plate preparation. Plates 20 × 20 cm with thin layers were prepared using a Camag applicator.

Silica gel layers. A slurry was obtained by adding 80 ml of redistilled water to 35 g of Silica Gel DF 5 (Camag) with a UV indicator and after mixing them thoroughly, this was immediately used to coat the plates with a layer 300 μ thick. The plates were dried for 30 min at room temperature and then heated for 24 h at 120° in an oven. The plates were then cooled and stored in a desiccator for at least 24 h before use.

Kieselguhr layers. In the same way a slurry was obtained by adding 100 ml of redistilled water to 50 g of Kieselguhr G (Merck). The plates were dried for 30 min at room temperature and then heated for 60 min at 110–120° in an oven. The plates were cooled and stored in a desiccator for at least 4 h before use. The impregnation of Kieselguhr thin layers was made in a chromatography chamber by allowing a solution of β-phenoxyethanol in benzene to ascend the plate by capillary action. Benzene was then allowed to evaporate into the air from the layer at room temperature.

Chromatographic procedure. Pure samples of chlorinated *p*-benzoquinones were applied at the starting line. After drying the spots at room temperature, the plates were placed in developing chambers saturated with solvents and developed by an ascending method, until the solvent front had travelled 15 cm beyond the original spots. The plates were removed from the chambers and, after marking the solvent front, allowed to dry in air. During the experiments the temperature was 24 ± 0.5°.

Detection. All spots on silica gel layers were located in UV light (D_1), but the spots on kieselguhr were revealed using chemical detection (D_2). D_1 = UV light (254 nm) — quenching spots; D_2 = solution of 0.1 N $AgNO_3$ – 5 N NH_4OH (1:1) — dark brown spots.

Results and discussion

Many solvent combinations were examined for developing the chromatograms on Silica Gel DF 5 and Kieselguhr G; the best of these were found to be: S_1 = a 25 % solution of benzene in carbon tetrachloride; S_2 = a saturated solution of β-phenoxyethanol in *n*-hexane. The saturated solutions of β-phenoxyethanol in *n*-heptane and *n*-octane were also examined.

The R_F values of chlorinated *p*-benzoquinones in the solvent system used are given in Table II. A 25 % solution of benzene in carbon tetrachloride has been found to be the most satisfactory developing system both for identification and separation of these compounds on silica gel. The characteristic shades of chlorinated derivatives of *p*-benzoquinone in UV light provide a means for their quick and satisfactory identification. It was found that silica gel gave much better and reproducible R_F values than

TABLE II

R_F VALUES OF SOME CHLORINATED DERIVATIVES OF *p*-BENZOQUINONE

Compound	*Silica Gel,* S_1	*Kieselguhr*[a], S_2
1,4-Benzoquinone	0.14	—
2-Chloro-1,4-benzoquinone	0.23	0.39
2,3-Dichloro-1,4-benzoquinone	0.30	0.32
2,5-Dichloro-1,4-benzoquinone	0.37	0.36
2,6-Dichloro-1,4-benzoquinone	0.40	0.41
2,3,5-Trichloro-1,4-benzoquinone	0.53	0.29
2,3,5,6-Tetrachloro-1,4-benzoquinone	0.73	0.24

[a] = Impregnation: 4% β-phenoxyethanol in benzene.

kieselguhr. The R_F values of 2,6-dichloro-1,4-benzoquinone, 2,3,5-trichloro-1,4-benzoquinone and chloranil obtained on silica gel layers are different and allow satisfactory identification and separation of these compounds.

Better separation of 2,6-dichloro-1,4-benzoquinone and 2,5-dichloro-1,4-benzoquinone was obtained on kieselguhr impregnated with solutions of β-phenoxyethanol in benzene, using its saturated solution in *n*-hexane as the mobile phase. The optimal separation of chlorinated *p*-benzoquinones on kieselguhr was obtained, when the concentration of β-phenoxyethanol in impregnation solution was 3.2 to 6.0 %.

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1 K. SUZUKI AND S. KATO, *Eisei Shinkenjo Kenkyu Hokoku*, 81 (1962) 51.
2 J. ELIÁŠEK AND A. JUNGWIRTH, *Collection Czech. Chem. Commun.*, 28 (1954) 2163.
3 T. SPROSTON, *Anal. Chem.*, 26 (1954) 552.
4 J. B. CONANT AND L. F. FIESER, *J. Am. Chem. Soc.*, 45 (1923) 2201.
5 A. ECKERT AND R. ENDLER, *J. Prakt. Chem.*, 104 (1922) 82.
6 S. LEVY AND G. SCHULTZ, *Ann. Chem.*, 210 (1881) 148.
7 J. GUARESCHI AND G. DACCOMO, *Chem. Ber.*, 18 (1885) 1170.
8 H. BILTZ AND W. GIESE, *Chem. Ber.*, 37 (1904) 4009.
9 A. SCHAEFFER AND D. SCHULZE, *Ger.* (*East*) *Pat.*, 12 224 (1956).

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A modified detection of triazine herbicide residues and their hydroxy-derivatives on thin-layer chromatograms

For the serial investigation of triazine herbicides, thin-layer chromatography (TLC) is the most suitable method at present. The detection of substances separated on the chromatogram has been tried by several methods described earlier in the literature. Among these chlorination and subsequent reaction with iodine starch proved to be the most sensitive[1]. The use of chlorine gas and some other factors, however, make the widespread application of this method difficult. Therefore, based on this reaction, a method has been developed that, besides being sensitive, might be easily and safely applied. This method is also suggested for the detection of certain triazine transformation products, hydroxy derivatives in particular.

The chlorination of triazines was performed by submersion of the layer into a carbon tetrachloride solution containing chlorine instead of chlorine gas. The potassium iodide starch solvent was substituted by a potassium iodide–*o*-tolidine solution[2] which can be stored well.