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SEPARATION OF ALKYL 2,5-DICHLORO-4,6-DINITROPHENYL CARBONATES BY GAS CHROMATOGRAPHY

PAVEL VÝBOH, MILAN MICHÁLEK AND JOZEF DOLEŽAL

Research Institute of Agrochemical Technology, Bratislava (Czechoslovakia)

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SUMMARY

The conditions for the separation of alkyl 2,5-dichloro-4,6-dinitrophenyl carbonates are described. It was possible to carry out the separation using Methyl Silicone Polymer SE-30 and Silicone Oil QF-1 on Chromosorb W with both isothermic and programmed temperatures. The conditions described can also be used for quantitative analysis.

INTRODUCTION

Some alkyl aryl carbonates are known to have a remarkable biological effect¹⁻¹⁰, e.g. alkyl 2,5-dichloro-4,6-dinitrophenyl carbonates possess a high fungicidal activity¹¹. During investigations on the relationship between the biological activity and the structure of these compounds, their behaviour in gas-liquid chromatography (GLC) was studied. The use of GLC for separation and identification purposes, and the determination of suitable experimental conditions for quantitative analysis were investigated.

The problem of separating chlorinated, nitrated and chloro-nitro derivatives of benzene by gas chromatography has been dealt with adequately in the literature. For example, chloronitrobenzenes¹², nitrophenols¹³, 2,4-dinitrophenylhydrazones¹⁴, 2-alkyl-4,6-dinitrophenols, and 4-alkyl-2,6-dinitrophenols¹⁵ were determined by this method. Attempts were made to use gas chromatography as a selective analytical method for alkyl 2-phenyl-4,6-dinitrophenyl carbonates¹⁶ and alkyl 2,4-dinitro-6-*sec.*-butylphenyl carbonates¹⁷.

EXPERIMENTAL

Preparation of alkyl 2,5-dichloro-4,6-dinitrophenyl carbonates

Alkyl 2,5-dichloro-4,6-dinitrophenyl carbonates were prepared by the reaction of corresponding esters of chloroformic acid with 2,5-dichloro-4,6-dinitrophenol in the presence of an HCl acceptor¹⁸. The purity of the standards was tested chromatographically.

Apparatus and working conditions

The Fractovap model D gas chromatograph¹ (Carlo Erba, Milan) equipped with a flame ionization detector was used. Boron silicate glass columns, 85 cm in length and 0.25 cm in diameter, were used. The chromatography of a carbonate mixture was carried out under the following conditions:

(A) 3% Methyl Silicone Polymer SE-30 on Chromosorb W (60–80 mesh), temperatures 175° and 200° at nitrogen carrier gas flow rates of 93 ml/min and 25 ml/min, respectively.

(B) 5% Silicone Oil QF-1 on Chromosorb W (60–80 mesh), temperatures 175° and 200° at nitrogen carrier gas flow rates of 93 ml/min and 52 ml/min, respectively.

In both cases, the injection block temperature was 210°, the hydrogen pressure 0.3 kp/cm² and the oxygen pressure 0.6 kp/cm². In addition to the separation at an isothermic temperature, separations were carried out with a linearly programmed temperature at different carrier gas flow rates, different rates of temperature increases and different initial temperatures. The injection block temperature and the hydrogen and oxygen pressures were the same as during the separation at the isothermic temperature. 0.2–0.5 μ l of a 2–3% solution of carbonates in acetone were injected, using a 10 μ l Hamilton microsyringe.

TABLE I

RELATIVE ELUTION TIMES OF ISO- AND *n*-ALKYL 2,5-DICHLORO-4,6-DINITROPHENYL CARBONATES

R	A (3% SE-30)		B (5% QF-1)	
	175°	200°	175°	200°
—CH ₃	0.24	0.31	0.34	0.39
—C ₂ H ₅	0.31	0.35	0.40	0.45
—C ₃ H _{7-i}	0.35	0.38	0.42	0.46
—C ₃ H ₇	0.44	0.49	0.54	0.57
—C ₄ H _{9-i}	0.56	0.58	0.61	0.63
—C ₄ H ₉	0.66	0.70	0.72	0.74
—C ₅ H _{11-i}	0.83	0.82	0.86	0.85
—C ₅ H ₁₁	1.00	1.00	1.00	1.00
—C ₆ H ₁₃	1.50	1.44	1.38	1.31
—C ₇ H ₁₅	2.25	2.04	1.88	1.74
—C ₈ H ₁₇	3.37	2.90	2.59	2.30
—C ₉ H ₁₉	5.00	4.14	3.55	3.04
—C ₁₀ H ₂₁	7.43	5.86	4.82	4.55

RESULTS AND DISCUSSION

The relative elution times of *n*- or iso-alkyl 2,5-dichloro-4,6-dinitrophenyl carbonates, referred to *n*-pentyl carbonate, are shown in Table I. The relative elution times of some other carbonates, 2,5-dichloro-4,6-dinitrophenyl carbonates and 2,5-dichloro-4-nitrophenyl carbonates, referred to ethylmercaptoethyl 2,5-dichloro-4,6-dinitrophenyl carbonate, are shown in Table II.

The chromatogram of a synthetic mixture of *n*-alkyl 2,5-dichloro-4,6-dinitrophenyl carbonates is illustrated in Fig. 1. Fig. 2 shows the chromatogram of other carbonates.

TABLE II

RELATIVE ELUTION TIMES OF SOME OTHER ALKYL AND ARYL 2,5-DICHLORO-4,6-DINITROPHENYL CARBONATES AND ALKYL 2,5-DICHLORO-4-NITROPHENYL CARBONATES

Carbonates	3% SE-30 (170°)
Methyl 2,5-dichloro-4-nitrophenyl carbonate	0.61
Ethyl 2,5-dichloro-4-nitrophenyl carbonate	0.82
Ethylmercaptoethyl 2,5-dichloro-4,6-dinitrophenyl carbonate	1.00
Allyl 2,5-dichloro-4,6-dinitrophenyl carbonate	1.59
Propargyl 2,5-dichloro-4,6-dinitrophenyl carbonate	1.59
Ethylthio 2,5-dichloro-4,6-dinitrophenyl carbonate	2.41
Chloroethyl 2,5-dichloro-4,6-dinitrophenyl carbonate	3.09
Benzyl 2,5-dichloro-4,6-dinitrophenyl carbonate	5.86
Cyclohexyl 2,5-dichloro-4,6-dinitrophenyl carbonate	7.08

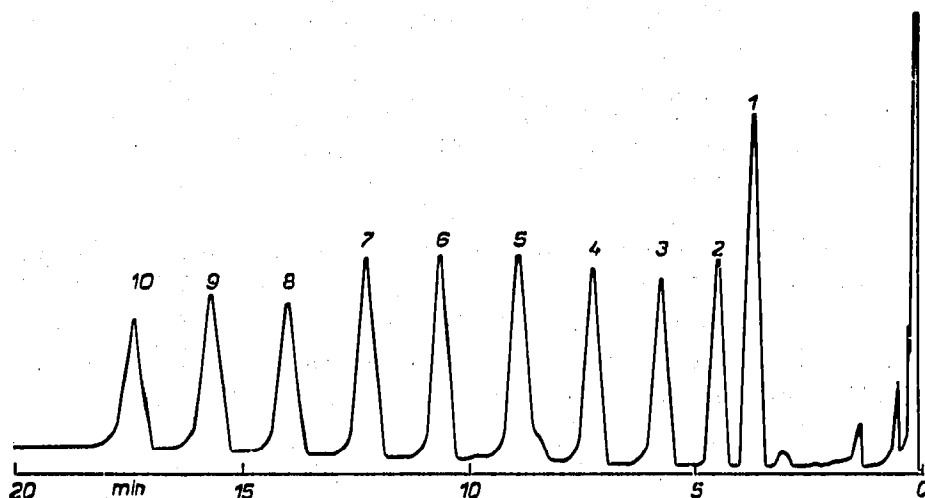


Fig. 1. Chromatogram of the synthetic mixture of *n*-alkyl 2,5-dichloro-4,6-dinitrophenyl carbonates. Alkyl groups: 1 = methyl; 2 = ethyl; 3 = propyl; 4 = butyl; 5 = pentyl; 6 = hexyl; 7 = heptyl; 8 = octyl; 9 = nonyl; 10 = decyl. Conditions: temperature, 130–220°, 4.5°/min; nitrogen flow rate, 97 ml/min; stationary phase, 3% SE-30.

The working conditions suitable for obtaining symmetrical peaks during chromatography with programmed temperature are described in the legends to Figs. 1 and 2. Under other conditions, the separation of methyl and ethyl carbonates could not be carried out satisfactorily.

The dependence of the specific elution volume on the number of carbon atoms in the *n*- or iso-alkyl radical 2,5-dichloro-4,6-dinitrophenyl carbonates on columns A and B is shown in Fig. 3. In both cases, the exceptional position of the first member of the homologous series was observed.

Peaks of separated components, obtained by chromatography on columns A and B are symmetrical. SE-30 seems to be more suitable for quantitative analysis at 170° and at a gas flow rate of about 100 ml/min. With QF-1 the separation is not so good and the elution times are longer.

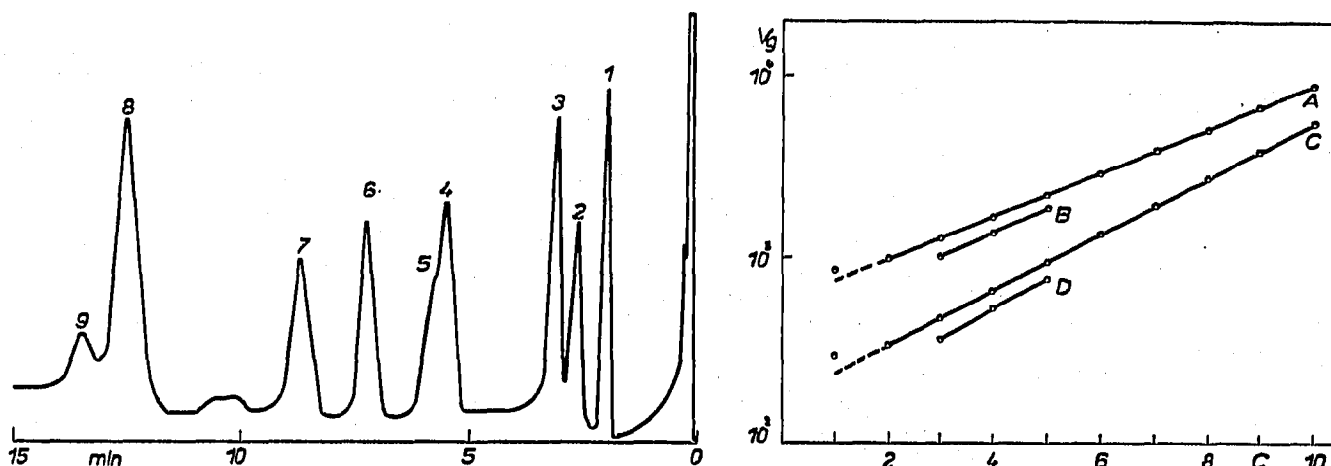


Fig. 2. Chromatogram of some other alkyl and aryl 2,5-dichloro-4,6-dinitrophenyl carbonates and alkyl 2,5-dichloro-4-nitrophenyl carbonates. 1 = Methyl and 2 = ethyl 2,5-dichloro-4-nitrophenyl carbonate; 3 = ethylmercaptoethyl, 4 = allyl, 5 = propargyl, 6 = ethylthio, 7 = chloroethyl, 8 = benzyl, and 9 = cyclohexyl 2,5-dichloro-4,6-dinitrophenyl carbonate. Conditions: temperature, 140–200°, 3°/min; nitrogen flow rate, 109 ml/min; stationary phase, 3% SE-30.

Fig. 3. Dependence of the specific elution volume (V_g) on the number of carbon atoms of the alkyl group in *n*-alkyl 2,5-dichloro-4,6-dinitrophenyl (A and C) and isoalkyl 2,5-dichloro-4,6-dinitrophenyl carbonates (B and D), respectively. Columns: 3% SE-30 on Chromosorb W at 175° (C and D), 5% QF-1 on Chromosorb W at 200° (A and B).

For the separation of the carbonates mentioned, some other stationary phases were tested, *viz.* butanediol succinate (BDS) with H_3PO_4 on Chromosorb W, Methyl Silicone Polymer SE-30 with Igepal CO 880 on silanized Chromosorb W, cyclohexane-dimethanol succinate (CHDMS) with H_3PO_4 on silanized Chromosorb W, Silicone Grease E 301 on Chromosorb W, Silicone Oil F 60 on Chromosorb W, Apiezon L (APL) with Igepal CO 880.

On columns with APL and Igepal CO 880, the carbonates were not eluted. On the other above-mentioned phases, the separation can be carried out, but it is not satisfactory and the peaks obtained are asymmetrical.

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