Journal of Chromatography, 288 (1984) 233–235
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,523

Note

Reversed-phase thin-layer chromatographic behaviour of some diethyl phenylphosphates

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(Received December 15th, 1983)

Although a large number of organophosphate esters have been analysed[1,2] by thin-layer chromatography (TLC), most of these separations were achieved by using a normal phase (generally silica gel G). However, there are a few reports[3,4] on the reversed-phase TLC (RP-TLC) separation of these compounds.

We report here the systematic RP-TLC of a series of diethyl phenylphosphates having the general structure shown in Fig. 1. The separation of these compounds is difficult by normal phase TLC, and no RP-TLC data for them have yet been reported.

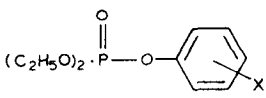
EXPERIMENTAL

The diethyl phenylphosphates were synthesised by the reported method[5]. Their purity was more than 99% as determined by gas chromatography.

In order to study the effects of the amount of impregnator on the RP-TLC separation, solutions containing 1–10% *n*-octanol in hexane were prepared and a number of plates coated with silica gel G were impregnated with each solution. The plates were well dried at 30°C for 8 h before use. Initially, a few representative phosphates were selected and spotted.

For all the TLC experiments, water–acetone (60:40, v/v) was used as eluent. This composition was found suitable after comparing the results with compositions of 100:0, 80:20, 50:50, 30:70 and 20:80 (v/v). The solvent fronts were allowed to travel distances up to 10 cm. The compounds were detected using iodine vapours. The experiments were carried out in triplicate. The deviations in the R_F values were not more than ± 0.02 in all cases.

The separation of all the phosphates was then carried out under optimum conditions on the two RP-TLC systems: (1) silica gel G impregnated with 1.5% *n*-octanol in hexane; (2) silica gel G impregnated with 1.5% SE-30 silicone oil (Merck,



X = $-CH_3$, $-Cl$, $-Br$, $-CN$, $-NO_2$

Fig. 1. Chemical structure of diethyl phenylphosphate esters.

0021-9673/84/$03.00

TABLE I

EFFECTS OF VARIATION OF IMPREGNATOR AMOUNT ON THE RP-TLC SEPARATION OF DIETHYL PHENYLPHOSPHATE ESTERS

Mobile phase: water–acetone (60:40, v/v). Values quoted are $R_F \pm 0.02$.

Compound No.	*Substituent X (see Fig. 1)*	*Percentage of n-octanol in hexane impregnated*				
		1	*1.5*	*2*	*4*	*5*
2	3-Me	0.22	0.22	0.20	0.19	0.17
3	4-Me	0.30	0.30	0.28	0.22	0.16
4	2-Cl	0.24	0.24	0.22	0.16	0.15
5	3-Cl	0.19	0.18	0.17	0.15	0.14
9	4-CN	0.31	0.33	0.26	0.23	0.24
10	4-NO_2	0.24	0.24	0.22	0.21	0.21

Darmstadt, F.R.G.) in ethanol. A normal phase separation using silica gel G was also carried out. All other experimental conditions were as described above. The R_F values obtained with various amounts of impregnator for a few representative esters are given in Table I. The R_F values for all the phosphates studied on the two RP-TLC systems at the optimum amount of impregnator and on the normal phase TLC system are given in Table II. The R_M values calculated in the usual manner[6] are also reported. ΔR_M values were calculated with reference to diethyl phenylphosphate as reference compound.

RESULTS AND DISCUSSION

In RP-TLC systems the separation depends upon the amount of impregnator employed. In most of the reported work[7] it has been found that 5–10% (v/v) impregnator solution enables the required separation. In the present study our interest lays in the optimum concentration of impregnator for the separation of phosphate esters, since systematic studies on series of such compounds have not previously been carried out.

We initially studied the effect of impregnator amount using a few representative esters which differed in the nature of the substituent X or which were poorly separated on normal phase TLC. These compounds were poorly separated on a plate impregnated with 10% *n*-octanol as compared with one impregnated with 5% *n*-octanol. Therefore we studied the separation using still lower amounts of impregnator. The R_F values for 1–5% impregnation reported in Table I indicate clearly the improvement in separation with lower ($< 2\%$) amounts of impregnator. For example, in the case of compounds 2 and 3 the R_F values differ by 0.01 on a 5% impregnated plate, but by 0.08 on a 1.5% impregnated plate. Further, it is seen from the data in Table I that the R_F values for any particular compound with 1%, 1.5% and 2% impregnation are similar. For example, in the case of compound 10 the R_F value changes only from 0.24 to 0.22 when the impregnator amount changes from 1 to 2%. This means that the reproducibility of R_F values at lower percentage impregnations is little affected by the combined effects of adsorption and partition processes which generally occur at low impregnator amounts.

TABLE II

NORMAL AND RP-TLC SEPARATION OF DIETHYL PHENYLPHOSPHATE ESTERS USING WATER–ACETATE (60:40, v/v) AS MOBILE PHASE

Compound No.	*Substituent X (see Fig. 1)*	*Normal phase R_F (± 0.02)*	*Reversed phase (1.5% n-octanol)*			*Reversed phase (1.5% SE-30)*		
			R_F (± 0.02)	R_M	ΔR_M*	R_F (± 0.02)	R_M	ΔR_M*
1	–	0.38	0.42	0.14	0.00	0.54	−0.07	0.00
2	3-Me	0.50	0.22	0.55	0.41	0.43	0.12	0.19
3	4-Me	0.48	0.30	0.37	0.23	0.47	0.05	0.12
4	2-Cl	0.56	0.24	0.50	0.36	0.34	0.29	0.36
5	3-Cl	0.60	0.18	0.66	0.52	0.30	0.37	0.44
6	4-Cl	0.61	0.20	0.60	0.46	0.27	0.43	0.50
7	3-Br	0.57	0.15	0.75	0.61	0.32	0.33	0.40
8	4-Br	0.58	0.12	0.87	0.73	0.37	0.23	0.30
9	4-CN	0.47	0.33	0.31	0.17	0.51	0.02	0.09
10	4-NO_2	0.49	0.24	0.50	0.36	0.40	0.18	0.25

* ΔR_M values refer to the substituents on the phenyl ring.

Table II compares the R_F values obtained in both RP-TLC systems with those in normal phase TLC for all the phosphates on silica gel G. Many positional isomers are poorly separated on the normal phase, but show improved separation on RP-TLC with both the impregnators studied. For example, for compounds 9 and 10 the R_F values on the normal phase differ by only 0.02, but RP-TLC with 1.5% *n*-octanol and with 1.5% SE-30 yielded differences in R_F of 0.09 and 0.11 units respectively, well outside the experimental error of 0.02.

There is a considerable change in R_M value with the nature of the substituent on the phenyl ring. In both RP-TLC systems there is a decrease in R_F value of parent compound of the series, *i.e.*, diethyl phenylphosphate (1) upon substitution by various groups.

In conclusion, our results indicate that lower impregnator amounts (<2%) improve the separation of organophosphate esters by RP-TLC, and that the separation is poor at >5% impregnator, unlike most of reported RP-TLC separations.

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