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Products of the Reaction between Alcohols and Phosphorus Pentoxide: II. Chromatographic Separation of the Products*

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Summary

Various solvents and operating conditions were investigated for paper-chromatographic separation of the various esters in the mixture obtained by the reaction $P_4O_{10} + 4ROH$. Optimum separation was obtained with a propanol–isobutanol–water–ammonia solvent at 10° during 16 hr and perchloric acid–ammonium molybdate developer. These conditions were found to produce complete separation in all investigated mixtures, independently of the nature of the organic chain in the esters. Preparative separation of the various products was obtained by column chromatography, using the same solvent as in paper chromatography on a cellulose-packed column.

As a first step in the identification of the various products of the reaction $P_4O_{10} + 4ROH$, it was important to determine how many of the 34 possible compounds (*1*) were in fact present in the resulting mixture. Paper chromatography was chosen for this purpose, since this method had already been used for both separation of orthophosphoric esters (*2*) and separation of inorganic ortho-, pyro-, poly-, and metaphosphates (*3*). Several other papers (e.g., Refs. *4,5,6,7*) deal with paper-chromatographic separation of organophosphorus compounds, but in general they concern mixtures of a

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* Part of the Ph.D. thesis of M. Zangen, Hebrew University, Jerusalem, April 1965.

different kind, mostly polyphosphate esters of higher alcohols containing additional functional groups. While this work was in progress, paper chromatography (with another solvent) was used successfully for separation of several methyl ortho- and pyrophosphates (*8*)—from a mixture obtained by different means, however.

Several variations in solvent composition, developer, separation time, and temperature were tried in order to obtain optimum separation of the products from the reaction $P_4O_{10} + 4C_8H_{17}OH$ (*n*-octanol). After this had been obtained, the same conditions were used to separate the products yielded by the reaction of phosphorus pentoxide with other alcohols. Finally, attempts were made to separate larger amounts of the various esters by column chromatography.

EXPERIMENTAL

The ester mixtures were prepared as described in Part I of this series (*1*). After adequate dilution of the ester mixture with kerosene, acetone, or dioxane (the last two in the case of alcohols containing four carbon atoms or less), a 5-μl drop of solution containing about 30 μg of P was placed on a 40 × 5 cm strip of Whatman No. 1 chromatographic paper, and ascending chromatography was performed. The paper had previously been washed successively with dilute acetic acid, dilute ammonia, and water, then dried. After the chromatographic separation had proceeded for a fixed time, the paper was dried in a hot-air stream, sprayed with developer, dried, and treated in an oven at 70°C for 5 min. Ultraviolet irradiation then caused the appearance of green, blue, or violet spots (molybdenum blue, obtained by reduction of the phosphomolybdic complex).

Column chromatography was carried out in 30-cm glass columns of 0.8 cm in diameter, filled with Solca-Flox Cellulose. This was first washed with dilute acetic acid and then with the alkaline solvent that was found optimal in paper chromatography (see below). On the top of the column, 1 ml of a kerosene or dioxane solution of the ester mixture was added, its nomial concentration (i.e., the concentration calculated as if it contained only dialkyl pyrosphosphate) being 0.5 *M*; the alkaline solvent was then passed through.

RESULTS

The optimum conditions for separation of the products from the reaction $P_4O_{10} + 4C_8H_{17}OH$ were found to be:

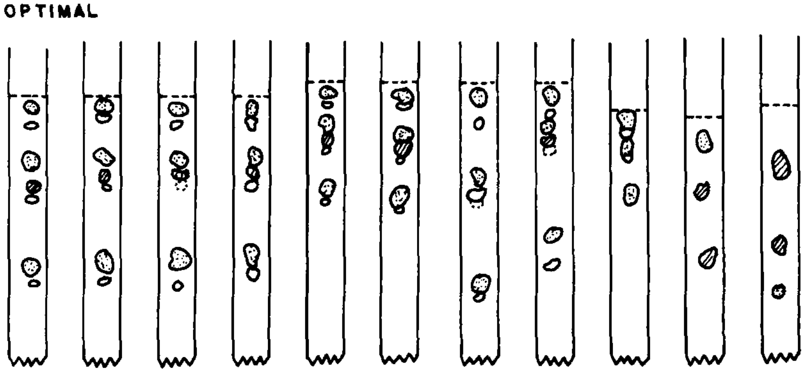

FIG. 1 FIG. 2 FIG. 3 FIG. 4 FIG. 5 FIG. 6 FIG. 7 FIG. 8 FIG. 9 FIG. 10 FIG. 11

FIGS. 1-11.

Solvent: 40% propanol, 15% isobutanol, 40% water, 5% ammonium hydroxide

Separation time: 16 hr

Temperature: 10°

Developer: 3% $HClO_4$, 3% HCl, 1% $(NH_4)_4Mo_7O_{24}\cdot 4H_2O$, 93% H_2O

Figure 1 shows the chromatography obtained under these optimum conditions. Figures 2–11 show the chromatograms obtained by variations in the composition of the alkaline solvent as given in Table 1.

Acidic solvents were, according to the literature (2,3), expected to be at least as efficient as alkaline solvents. However, solvents of compositions given in Table 2 yielded the chromatograms shown

TABLE 1

Solvent composition, wt. %	Chromatogram
Isopropanol, 40; isobutanol, 15; NH_4OH, 5; H_2O, 40	2
Propanol, 30; isobutanol, 25; NH_4OH, 5; H_2O, 40	3
Propanol, 55; isobutanol, 25; NH_4OH, 5; H_2O, 40	4
Propanol, 55; isobutanol, 20; NH_4OH, 5; H_2O, 20	5
Propanol, 55; isobutanol, 20; NH_4OH, 2.5; H_2O, 22.5	6
Propanol, 40; isobutanol, 15; NH_4OH, 2.5; H_2O, 42.5	7
Propanol, 40; isobutanol, 15; NH_4OH, 10; H_2O, 35	8
Propanol, 40; isobutanol, 15; NH_4OH, 20; H_2O, 25	9
Pyridine 55; NH_4OH, 20; H_2O, 25	10
Pyridine 20; ethyl acetate, 40; H_2O, 40	11

TABLE 2

Solvent composition, wt. %	Chromatogram
Isopropanol, 70; trichloroacetic acid, 5; H_2O, 25	12
Isopropanol, 70; trichloroacetic acid, 2.5; H_2O, 27.5	13
Isopropanol, 70; trichloroacetic acid, 10; H_2O, 20	14
Isopropanol, 60; trichloroacetic acid, 7; H_2O, 33	15
Isopropanol, 60; trichloroacetic acid, 5; H_2O, 35	16
Isopropanol, 70; trichloroacetic acid, 4; H_2O, 25; NH_4OH, 1	17
Isopropanol, 50; trichloroacetic acid, 4; H_2O, 25; NH_4OH, 1; *t*-butanol, 20	18
Isopropanol, 40; trichloroacetic acid, 4; H_2O, 25; NH_4OH, 1; *t*-butanol, 30	19
Isopropanol, 50; oxalic acid, 5; H_2O, 25; *t*-butanol, 20	20
Isopropanol, 50; oxalic acid, 2.5; H_2O, 27.5; *t*-butanol, 20	21
Isopropanol, 40; oxalic acid, 2.5; H_2O, 27.5; *t*-butanol, 30	22
Isopropanol, 60; formic acid, 5; H_2O, 35; *t*-butanol, 30	23
Isopropanol, 40; formic acid, 5; H_2O, 35; *t*-butanol, 20	24
Isopropanol, 40; formic acid, 15; H_2O, 20; *t*-butanol, 25	25
Isopropanol, 50; formic acid, 15; H_2O, 10; *t*-butanol, 25	26
Isopropanol, 70; picric acid, 5; H_2O, 25; *t*-butanol, 25	27
Isopropanol, 70; picric acid, 2.5; H_2O, 27.5	28

in Figs. 12–28. Bidimensional chromatography, using, successively, alkaline solvent 1 and acid solvent 19, yielded the chromatogram in Fig. 29. Figures 30–34 show chromatograms obtained with the alkaline solvent 1 at 10°C on varying the time allowed for chromatographic separation, while Figs. 35–43 show the results of varying the temperature in 16 hr of chromatography with the same solvent.

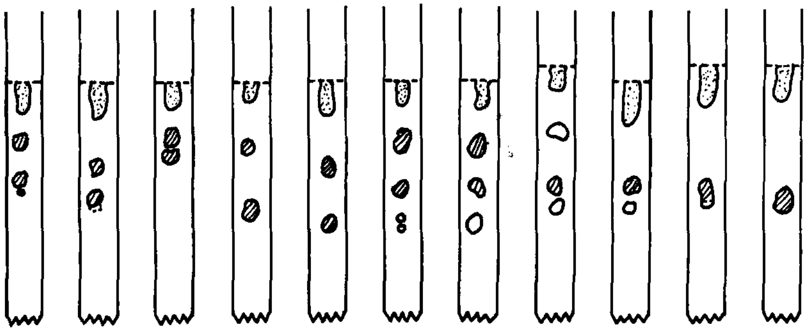

FIG.12 FIG.13 FIG.14 FIG.15 FIG.16 FIG.17 FIG.18 FIG.19 FIG.20 FIG.21 FIG.22

FIGS. 12–22.

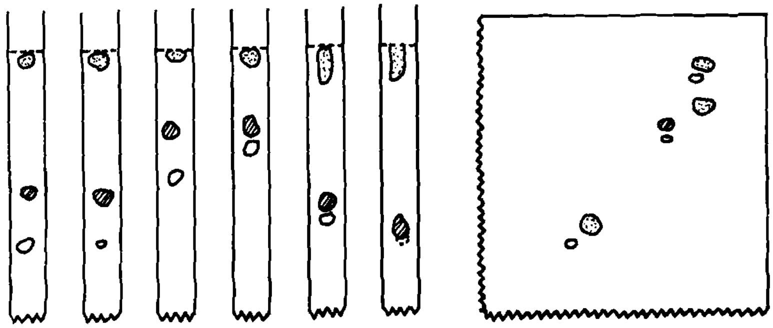

FIG.23 FIG.24 FIG.25 FIG.26 FIG.27 FIG.28 FIG.29

FIGS. 23–29.

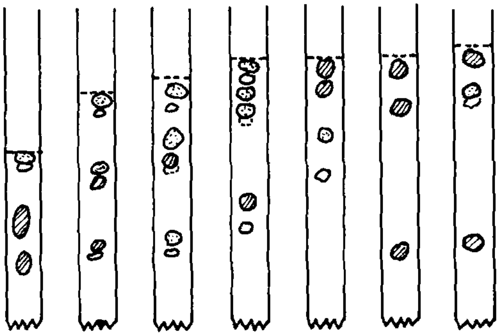

FIG.30 8 HR FIG.31 12 HR FIG.32 14 HR FIG.33 18 HR FIG.34 20 HR FIG.35 25°C FIG.36 20°C

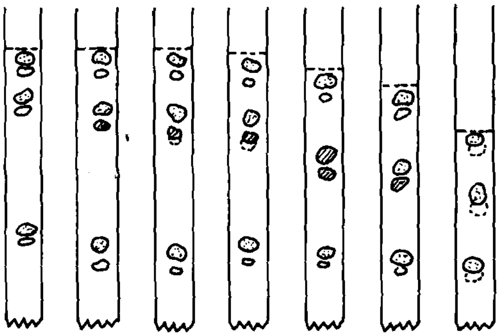

FIG.37 18°C FIG.38 15°C FIG.39 12°C FIG.40 8°C FIG.41 6°C FIG.42 3°C FIG.43 0°C

FIGS. 30–43.

In addition, a number of chromatograms were treated with developer solutions of different composition, especially of lower acidity, as used by Ebel (3), but no clear spots could be developed.

As can be seen from these figures, acid chromatography separates less compounds than alkaline chromatography, and the latter is not improved by bidimensional use of alkaline and acidic solvents.

It can further be seen that R_F values tend to increase with the basicity of the alkaline solvent, but in a different ratio, so that basicity that is too high will tend to merge various spots at the top of the chromatogram (while basicity that is too low will merge spots at the bottom). Similar effects are observed on increase of the ratio alcohol-water in the solvent, of the chromatographic separation time, or of the temperature.

Using the above optimum conditions for alkaline chromatography

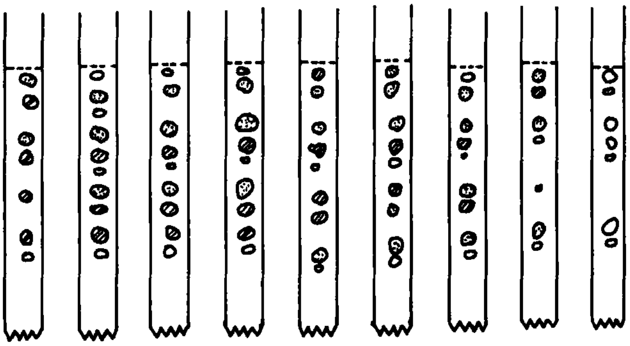

FIG.44 FIG.45 FIG.46 FIG.47 FIG.48 FIG.49 FIG.50 FIG.51 FIG.52

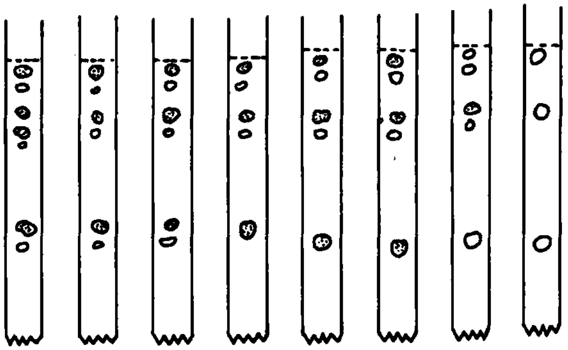

FIG.53 FIG.54 FIG.55 FIG.56 FIG.57 FIG.58 FIG.59 FIG.60

FIGS. 44–60.

TABLE 3

Alcohol	Number of C atoms	Chromatogram	Alcohol	Number of C atoms	Chromatogram
Methanol	1	44	2-Ethylhexanol	8	53
Ethanol	2	45	2,6-Dimethylheptanol	9	54
Propanol	3	46	3,3,5-Trimethylcyclohexanol	9	55
Isopropanol	3	47	1-Dodecanol	12	56
Butanol	4	48	6-Dodecanol	12	57
Isobutanol	4	49	2-Butyloctanol	12	58
sec-Butanol	4	50	2,6,8-Trimethylnonanol	12	59
Benzyl alcohol	7	51	3,9-Diethyltridecanol	17	60
Octanol	8	52			

of the octyl ester mixture, chromatographic separation was also carried out on the ester mixtures obtained from the reaction of P_4O_{10} with the alcohols enumerated in Table 3, yielding the chromatograms shown in Figs. 44–60. Thus it was possible to ascertain whether this separation method is suitable to ester mixtures independent of their chain length, branching, or cyclization. In addition, the underlined alcohols in Table 3 had been used (*9–11*) in reactions with phosphorus pentoxide for the synthesis of uranium extractants.

Subsequent spectrophotometric analysis (*12*) of the products separated by chromatography and their comparison with independently synthetized (poly)phosphate esters (*13*) showed each spot to correspond to one compound only, except for spot 5 from the methyl ester mixture. Results of the chromatographic separation are shown in Table 4. For the sake of brevity, only the ethyl esters (largest number of spots, 10), the diethyltridecyl esters (smallest number of spots, 3), and the components of mixtures used in solvent extraction are included in this table.

The identity of the various compounds was determined by their infrared spectra, using the method described in Part III of this series (*12*). This identification method was applied only to one out of every group of isomers, but since the chromatograms are very similar, it is assumed that the identification applied to the other isomers as well.

Attempts to separate the various compounds on the cellulose column itself, using the above developing solution on parts of the column, were unsuccessful, since no clear boundaries between the different compounds could be obtained. However, on passing 200

TABLE 4

Hydrocarbon group	Spot no.	R_F	Compound
Ethyl	1	0.96	Triethyl phosphate
	2	0.87	Diethyl phosphate
	3	0.80	Triethyl pyrophosphate
	4	0.72	Diethyl pyrophosphate
	5	0.63	Triethyl triphosphate
	6	0.54	Monoethyl phosphate
	7	0.45	Diethyl triphosphate
	8	0.38	Monoethyl pyrophosphate
	9	0.27	Diethyl trimetaphosphate
	10	0.18	Monoethyl trimetaphosphate
Octyl(2-ethylhexyl)	1	0.97	Trioctyl phosphate
	2	0.89	Dioctyl phosphate
	3	0.74	Dioctyl pyrophosphate
	4	0.63	Monooctyl phosphate
	5	0.54	Dioctyl triphosphate
	6	0.30	Dioctyl trimetaphosphate
	7	0.20	Monooctyl trimetaphosphate
Trimethylnonyl(2-butyloctyl)	1	0.98	Tri(trimethylnonyl)phosphate
	2	0.90	Di(trimethylnonyl)phosphate
	3	0.75	Di(trimethylnonyl)pyrophosphate
	4	0.65	Mono(trimethylnonyl)phosphate
	5	0.27	Mono(trimethylnonyl)trimetaphosphate
Diethyltridecyl	1	0.98	Tri(heptadecyl)phosphate
	2	0.75	Di(heptadecyl)pyrophosphate
	3	0.29	Mono(heptadecyl)trimetaphosphate

ml of the alkaline solvent through the column at a rate of 0.5 ml/min, complete separation of the various compounds was obtained, as was shown by paper chromatography of samples out of each 2-ml fraction in the eluate. Each chromatogram showed one spot only, and fractions yielding different spots were separated by at least one fraction yielding a blank chromatogram. These "blank" fractions were also found to be free of phosphorus compounds by regular analytical methods (*14*).

It may be noted that the mixture of methyl esters yields eight different compounds in column chromatography, but only seven in paper chromatography. Two compounds, which were later identified (*12*) as monomethyl phosphate and dimethyl triphosphate, are not separated by paper chromatography (see above); however, on elution from the cellulose column, a 2-ml fraction containing no phosphorus is collected between the fractions containing the former and latter compound.

REFERENCES

1. M. Zangen, Y. Marcus, and E. D. Bergmann, *Separation Sci.* **2**, 187 (1967).
2. C. S. Hanes and F. A. Isherword, *Nature,* **164**, 1107 (1949).
3. J. P. Ebel, *Bull. Soc. Chim. France,* **1953**, 991.
4. D. N. Bernhart and W. B. Chess, *Anal. Chem.,* **31**, 1026 (1959).
5. M. J. Smith, *Anal. Chem.,* **31**, 1023 (1959).
6. F. H. Pollard, G. Nickless, and R. W. Warrender, *J. Chromatog.,* **9**, 493 (1962).
7. F. H. Pollard, G. Nickless, and A. M. Bigwood, *J. Chromatog.,* **16**, 207 (1964).
8. H. A. Moule and S. Greenfield, *J. Chromatog.,* **11**, 77 (1963).
9. D. A. Ellis, *U.S.A.E.C. Rept. DOW-81* (1952).
10. R. H. Bailes and P. S. Long, *U.S.A.E.C. Rept. DOW-85* (1953).
11. Z. Hadari, *Israel A.E.C. Rept. M4/UP (RL.P) G-5* (1956).
12. M. Zangen, E. D. Bergmann, and Y. Marcus, *Israel J. Chem.,* **5**, 89 (1967).
13. M. Zangen, *Israel A.E.C. Rept. I.A. 1028* (1965).
14. F. Feigl, *Spot Tests in Organic Analysis,* Elsevier, Amsterdam, 1960, p. 99.

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