

Separation of lower oxo acids of phosphorus by paper chromatography

Twelve oxo acids of phosphorus with oxidation numbers lower than five have so far been isolated as alkali or ammonium salts which are stable in neutral aqueous solution. Several investigations¹⁻⁴ have been reported on the separation of anions of these oxo acids of phosphorus using paper chromatography. However, in all these investigations, only a limited number of these oxo acids of phosphorus have been treated as the objects of the analysis. The present investigation was undertaken to obtain information on behaviors of anions of all these oxo acids of phosphorus having low oxidation numbers, as well as orthophosphate, using paper chromatography.

Sodium or ammonium salts of P^1 , P^3 , P^3-O-P^3 , P^2-P^4 , $(-P^3-)_6$, $P^3-O-P^4-P^4$, $P^4-P^3-P^4$, P^3-O-P^5 , P^4-P^4 , $(-P^4-P^4-O-)_2$, $P^4-P^4-O-P^4-P^4$, $P^5-O-P^4-P^4$ and P^5 -acid were used. After the preliminary experiments on developing solvents, five acidic^{2,5-8} and seven basic solvents^{1,2,5,9-11}, reported by many investigators for the separation of anions of condensed phosphates and of oxo acids of phosphorus having low oxidation numbers, it was found that the following acidic and basic solvents are the most useful for the present purpose. The acidic solvent was composed of 325 ml of acetone, 25 g of trichloroacetic acid, 1.75 ml of a 28% aqueous ammonia and 150 ml of water. The basic solvent was composed of 190 ml of ethyl alcohol, 150 ml of isobutyl alcohol, 2.7 ml of a 28% aqueous ammonia and 225.3 ml of water. Filter paper (Toyo No. 51A) was cut into a sheet (21 × 18 cm), and one side with the length of 18 cm cut into six tongue-shaped ends. After about 5 μ l of the sample solution containing about 5 μ g P of each oxo acid of phosphorus per μ l was loaded, the chromatographic run was carried out in a rectangular battery jar at 5-7° using the ascending method. The paper sheet was sprayed with an acidic molybdate solution and was exposed to u.v. rays until the blue spots appeared.

Fig. 1 shows the schematic representation of the R_F values of anions of twelve lower oxo acids of phosphorus and orthophosphate. As for the acidic solvent, a good separation can be obtained for P^1 , $P^5-O-P^4-P^4$, $P^4-P^3-P^4$, $P^4-P^4-O-P^4-P^4$, $(-P^4-P^4-O-)_2$, $(-P^3-)_6$ and each one species in the groups of P^3 and P^5 and of P^4-P^4 and P^2-P^4 . However, P^3-O-P^3 , P^3-O-P^5 and $P^3-O-P^4-P^4$ cannot be identified because they are hydrolyzed at the position of the P-O-P bonds during the chromatographic run. Ring-formed $(-P^4-P^4-O-)_2$ is also partly hydrolyzed to chain-formed $P^4-P^4-O-P^4-P^4$.

On the other hand, the basic solvent does not give rise to any appreciable hydrolysis of the three oxo acids mentioned above. By the use of the basic solvent, P^1 , P^3-O-P^3 , P^3 , P^3-O-P^5 and $(-P^3-)_6$ give the separate spots on the chromatogram. However, the groups of $(-P^4-P^4-O-)_2$, P^5 , P^2-P^4 and $P^3-O-P^4-P^4$ and of P^4-P^4 , $P^5-O-P^4-P^4$, $P^4-P^3-P^4$ and $P^4-P^4-O-P^4-P^4$ appear at the similar positions on the chromatogram, respectively. Each species in the group of P^3 and P^5 or of P^4-P^4 and P^2-P^4 , which cannot be separated with the acidic solvent, gives the separate spot on the chromatogram developed with the basic solvent, respectively. P^3-O-P^3 and P^3-O-P^5 , which are hydrolyzed in the acidic solvent, also give the separate spots by the use of the basic solvent. However, $P^3-O-P^4-P^4$, which also is hydrolyzed in the acidic solvent, cannot be identified by the chromatographic run with the basic solvent, if $(-P^4-P^4-O-)_2$, P^5 or P^2-P^4 are present together.

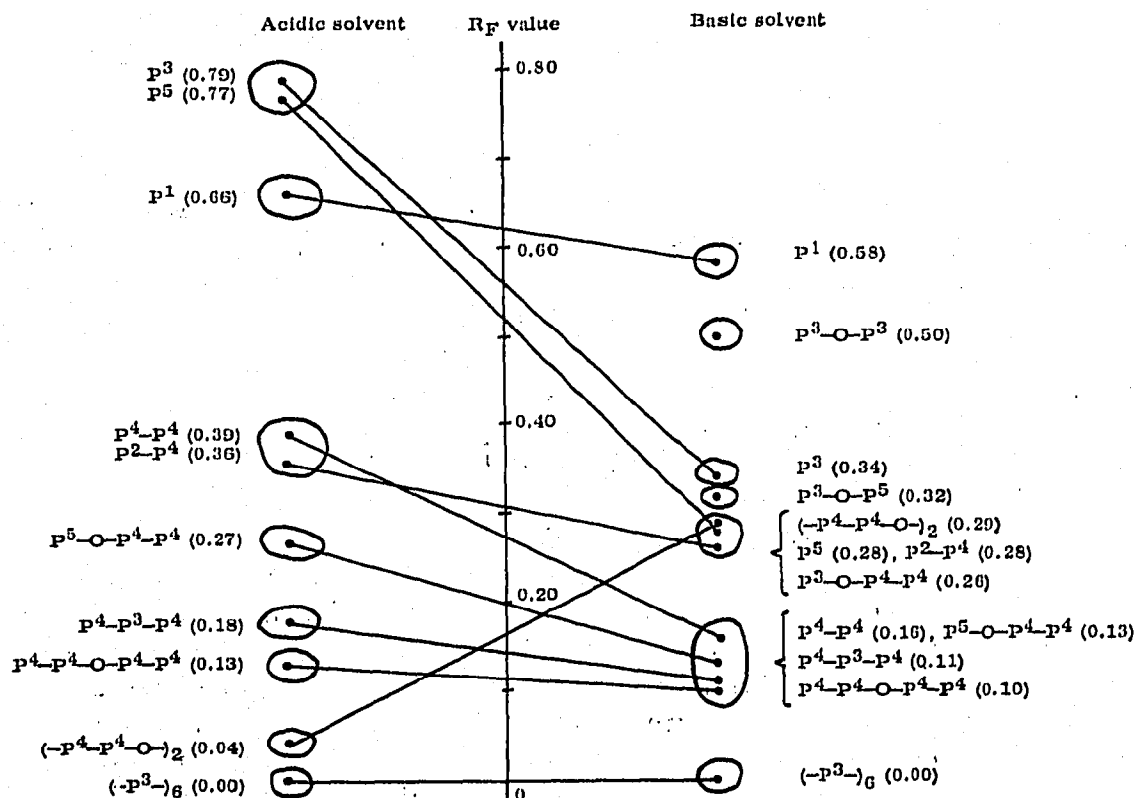


Fig. 1. R_F values of anions of twelve oxo acids having low oxidation numbers of phosphorus and orthophosphate.

All R_F values of the oxo acids of phosphorus obtained using the chromatography with the acidic solvent are higher than those with the basic solvent, except ring-formed $(-P^4-P^4-O)_2$. Although the reason for this characteristic behavior of $(-P^4-P^4-O)_2$ is unknown, similar behaviors have been observed for trimeta-, tetrameta- and higher members of ring-formed phosphates, which move faster in basic solvents than in acidic solvents when they are treated using paper chromatography.

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- 1 A. BONNIN AND P. SUE, *Compt. Rend.*, 239 (1952) 960.
- 2 Y. VOLMAR, J. P. EBEL AND Y. F. BASSILL, *Bull. Soc. Chim. France*, 20 (1953) 1085.
- 3 B. BLASER AND K.-H. WORMS, *Z. Anorg. Allgem. Chem.*, 300 (1959) 237, 250; 301 (1959) 7, 18; 311 (1961) 21; 312 (1961) 146.
- 4 H. HARNISCH, *Z. Anorg. Allgem. Chem.*, 300 (1959) 261.
- 5 E. THILO AND D. HEINZ, *Z. Anorg. Allgem. Chem.*, 281 (1955) 318.
- 6 D. N. BERNHART AND W. B. CHES, *Anal. Chem.*, 31 (1959) 1026.
- 7 R. M. KOLLOFF, *Anal. Chem.*, 33 (1961) 373.
- 8 O. PFRENGLE, *Z. Anal. Chem.*, 158 (1957) 81.
- 9 M. EBERT AND A. VARHANIKOVA, *Chem. Průmysl.*, 12 (1962) 192.
- 10 J. P. EBEL, *Bull. Soc. Chim. France*, 20 (1953) 991.
- 11 G. BIBERACHER, *Z. Anorg. Allgem. Chem.*, 285 (1956) 86.

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