Journal of Chromatography, 92 (1974) 207–209

CHROM. 7290

Note

Thin-layer chromatographic separation of phosphorus acids, pyroacids, amidic acids and diamides

SUSANA A. DE LICASTRO and MIGUEL A. RÚVEDA

Laboratorio Química Orgánica Especial CITEFA, Zufriategui y Varela, V. Martelli, Buenos Aires (Argentina)

(Received November 1st, 1973)

In the course of studies on the reaction of organophosphorus dichlorides with sulphoxides[1–5] it was necessary to follow the reaction paths and carry out some purity control tests. Thin-layer chromatography (TLC) proved to be a useful tool for the solution of these problems.

There are some papers dealing with the TLC of mono- and diesters of phosphoric acid[6], organophosphorus insecticides[7,8] and organophosphorus compounds[9–11], but most of the authors used paper chromatography to identify the phosphorus compounds[12,13]. The colour reaction used in these cases was that of Hanes and Isherwood[14].

We have found that during the phosphorylation reaction[1–4] and the decomposition of phosphoramidic acids[5], besides phosphorus pyroacids, phosphorus acids, phosphorus chloridic acids (isolated as phosphorus amidic acids) and phosphorus diamides were formed and it was necessary to determine the TLC behaviour of these compounds.

In the present communication cellulose and silica gel layers are reported in the separation of the above compounds using different solvents. The spots were developed with the Dittmer and Lester spray reagent[15].

EXPERIMENTAL

Chromatography

Silica gel G (Merck, Darmstadt, G.F.R.) layers, 0.25 mm thick, were activated by heating at 110° for 1 h. Cellulose layers were precoated (Merck) 0.10 mm thick. Before spraying the plates they were dried at 100° for 5 min and air-cooled. *tert.*-Butyl alcohol (Schuchart, München, G.F.R.), acetone (Sintorgan, Buenos Aires, Argentina) and *n*-hexane (Carlo Erba, Milan, Italy) were of chromatography grade. For silica gel layers two developing solvent systems were used: (A) acetone–*tert.*-butyl alcohol–ammonia–water (5:4:1:1) and (B) acetone–*n*-hexane (4:6); for cellulose layers solvent system C, *n*-propyl alcohol–ammonia–water (6:3:1), was used.

Detection

The Dittmer and Lester spray reagent was prepared as described[15]; it was compared with Phospray reagent (Supelco, Bellefonte, Pa., U.S.A.).

Materials

All the acidic compounds used were prepared as described in previous papers[4, 5] and used as their salts. Diamides were obtained by well known procedures[16].

Phosphorus acids, pyroacids and amidic acids were used as 1% aqueous solutions and phosphorus diamides as 1% ethanolic or chloroform solutions. Of each 10 μl were applied to the plates.

RESULTS

R_F values for phosphorus acids, phosphorus pyroacids, phosphorus amidic acids and phosphorus diamides are given in Table I.

From the data obtained it can be seen that in the presence of a mixture of phosphorus acids, pyroacids, amidic acids and diamides, the diamides run with the solvent front when solvents A and C are used, followed by phosphorus amidic

TABLE I

R_F VALUES OF PHOSPHORUS ACIDS, PYROACIDS, AMIDIC ACIDS AND DIAMIDES

Phosphorus compounds	*Silica gel*		*Cellulose, solvent C*
	Solvent A	*Solvent B*	
$\mathrm{Me{-}P(O)(OH)_2}$	0.00	0.00	0.15
$\mathrm{[Me{-}P(O)(OH)]_2O}$	0.05	0.00	0.30
$\mathrm{Me{-}P(O)(OH)NEt_2}$	0.30	0.00	0.57
$\mathrm{MeO{-}P(O)(OH)_2}$	0.00	0.00	0.15
$\mathrm{[MeO{-}P(O)(OH)]_2O}$	0.00	0.00	0.37
$\mathrm{MeO{-}P(O)(OH)NHC_6H_{11}}$	0.35	0.00	0.75
$\mathrm{Ph{-}P(O)(OH)_2}$	0.00		0.30
$\mathrm{[Ph{-}P(O)(OH)]_2O}$	0.12		0.62
$\mathrm{Ph{-}P(O)(OH)NHC_6H_{11}}$	0.55		0.72
$\mathrm{Ph{-}P(O)(NHC_6H_{11})_2}$	1.00	0.27	1.00
$\mathrm{PhO{-}P(O)(OH)_2}$	0.00		0.37
$\mathrm{[PhO{-}P(O)(OH)]_2O}$	0.25		0.71
$\mathrm{PhO{-}P(O)(OH)NHC_6H_{11}}$	0.60		0.85
$\mathrm{PhO{-}P(O)(NHC_6H_{11})_2}$	1.00	0.72	1.00
$p\text{-}\mathrm{MeC_6H_4O{-}P(O)(OH)_2}$	0.00		0.49
$[p\text{-}\mathrm{MeC_6H_4O{-}P(O)(OH)]_2O}$	0.20		
$p\text{-}\mathrm{MeC_6H_4O{-}P(O)(OH)NHC_6H_{11}}$	0.60		
$p\text{-}\mathrm{MeC_6H_4O{-}P(O)(NHC_6H_{11})_2}$	1.00	0.70	
$p\text{-}tert.\text{-}\mathrm{BuC_6H_4O{-}P(O)(OH)_2}$	0.00		0.75
$[p\text{-}tert.\text{-}\mathrm{BuC_6H_4O{-}P(O)(OH)]_2O}$	0.32		
$p\text{-}tert.\text{-}\mathrm{BuC_6H_4O{-}P(O)(OH)NHC_6H_{11}}$	0.64		
$p\text{-}tert.\text{-}\mathrm{BuC_6H_4O{-}P(O)(NHC_6H_{11})_2}$	1.00	0.73	
$p\text{-}\mathrm{O_2NC_6H_4O{-}P(O)(OH)_2}$	0.00		0.49
$[p\text{-}\mathrm{O_2NC_6H_4O{-}P(O)(OH)]_2O}$	0.35		
$p\text{-}\mathrm{O_2NC_6H_4O{-}P(O)(OH)NHC_6H_{11}}$	0.62		
$p\text{-}\mathrm{O_2NC_6H_4O{-}P(O)(NHC_6H_{11})_2}$	1.00	0.62	

acids, phosphorus pyroacids, and finally phosphorus acids. On the silica layers, phosphorus acids remain at the origin and in the case of alkylphosphorus compounds very low R_F values were obtained for the phosphorus pyroacids, so that they could only be poorly distinguished from the phosphorus acids. For aryl compounds such a problem did not exist, as higher R_F values were obtained for pyroacids in spite of the fact that acids do not move from the origin either.

In general, cellulose proved to be more useful, firstly because acids and pyroacids are better separated and secondly because all the R_F values are higher and acids move from the starting point and can be separated from the polyacids that are sometimes present.

Phosphorus diamides are well resolved from the mixture but cannot be identified in this way as they run with the solvent front. Solvent B gave better results. As this solvent was a less polar one, acids did not move from the origin and two-dimensional development can be useful when diamides are present.

The spots were developed instantaneously with both reagents, giving blue spots on a white background for phosphorus acids, amidic acids and diamides and violet spots (that faded out) for phosphorus pyroacids; that is to say P–O and P–N bonds could be distinguished from P–O–P bonds.

ACKNOWLEDGEMENT

We thank the Consejo Nacional de Investigaciones Científicas y Técnicas for financial support.

REFERENCES

1 M. A. Rúveda, E. N. Zerba and E. M. de Moutier Aldao, *Tetrahedron*, 28 (1972) 5011.
2 M. A. Rúveda, E. N. Zerba and E. M. de Moutier Aldao, *Tetrahedron*, 29 (1973) 585.
3 M. A. Rúveda, E. N. Zerba and E. M. de Moutier Aldao, *An. Asoc. Quim. Argent.*, 61 (1973) 233.
4 M. A. Rúveda, S. A. de Licastro and E. M. de Moutier Aldao, to be published.
5 M. A. Rúveda and E. N. Zerba, to be published.
6 J. Stenersen, *J. Chromatogr.*, 54 (1971) 77.
7 J. Stenersen, *J. Chromatogr.*, 38 (1968) 538.
8 O. Antoine and G. Mees, *J. Chromatogr.*, 58 (1971) 247.
9 A. Lamotte and J. C. Merlin, *J. Chromatogr.*, 38 (1968) 296.
10 A. Lamotte, A. Francina and J. C. Merlin, *J. Chromatogr.*, 44 (1969) 75.
11 A. Lamotte and J. C. Merlin, *J. Chromatogr.*, 45 (1969) 432.
12 N. Henrich and F. Cramer, *J. Amer. Chem. Soc.*, 87 (1965) 1121.
13 N. K. Hamer, *J. Chem. Soc.*, (1965) 46.
14 C. S. Hanes and F. A. Isherwood, *Nature (London)*, 164 (1949) 1107.
15 J. C. Dittmer and R. L. Lester, *J. Lipid Res.*, 5 (1964) 126.
16 E. Fluck, *Topics in Phosphorus Chemistry, Vol. 4, Phosphorus–Nitrogen Chemistry*, Wiley, New York, 1967, p.291.