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Note

The Dissociation, Distribution, and Dimerization Constants of Some Organophosphorus Acids

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In a previous paper[1] the values of the acid dissociation constants of several esters of orthophosphoric acid were given, as well as the values of their dimerization and distribution constants in chloroform. Recently some other organophosphorus acids have been prepared *i.e.* two phosphonic acid esters R(RO)POOH and two phosphinic acids R_2POOH and their characteristic constants determined. The values of these constants are given in Table I.

TABLE I

Organophosphorus acid	pK_a	$\log K_2$	$\log K_d$
di-*n*-butylphosphinic acid	3.29	4.50	—0.20
diphenylphosphinic acid	1.72	3.22	0.56
phenylester of phenylphosphonic acid	0.68	3.46	—0.34
p-tolylester of *p*-tolylphosphonic acid	0.92	3.90	1.10

In Fig. 1 the relationship between pK_a of these and previously investigated acids and $\Sigma\sigma$ is given. Here $\Sigma\sigma$ signifies the sum of the constants σ of both substituents. In contrast with the previous work[1] the σ values given by Kabatchnik[2] were used instead of those introduced by Hammett[3]. The former values are characteristic for the compounds of fivevalent phosphorus and differ considerably from those given by Hammett.

As shown in Fig. 1 the points for different organophosphorus acids fit a straight line very well, which confirms the validity of the Hammett equation. The slope of the straight line in Fig. 1 is 1.30, representing the value of the constant ϱ in Hammett equation for the organophosphorus acids in one molar perchlorate solution.

According to Fig. 1 the substituent constant σ for *p*-chlorophenyl group in organophosphorus compounds is —0.04, for benzyl group —0.23 and for β-naphthyl group —0.24, respectively.

EXPERIMENTAL

Investigated monoesters of phosphonic acid R(RO)POOH have been prepared by partial hydrolysis of the corresponding phosphonic acid diesters in alcaline medium[4], while diesters have been obtained by the reaction between phosphoric acid diester chloride and the corresponding Grignard reagent. Phosphinic acids are hydrolytic products of the compounds obtained by the reaction between $POCl_3$ and Grignard reagent in the presence of pyridine[5].

The method used to determine the characteristic constants of the investigated acids has been published previously[1,6].

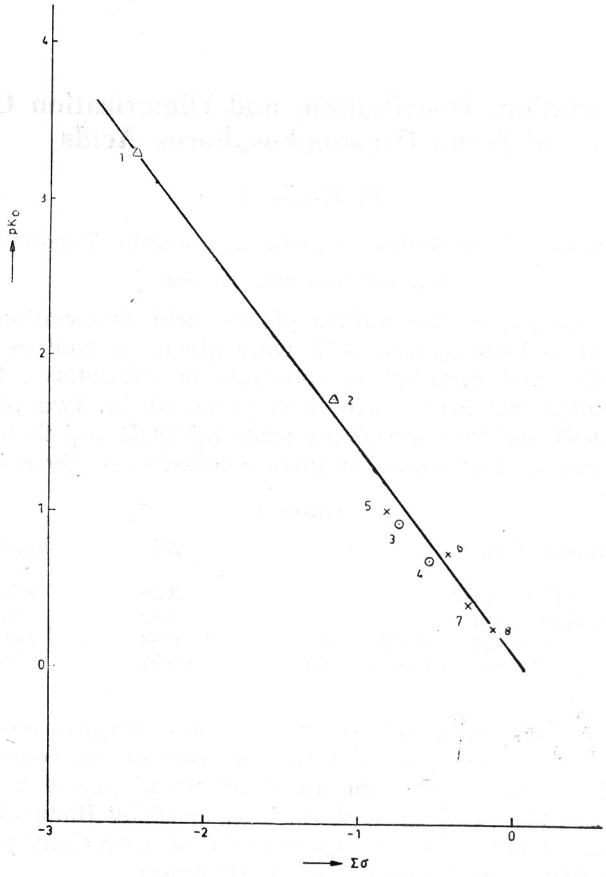

Fig. 1. Relationship between pK_a of some organophosphorus acids and $\Sigma\sigma$ of their substituents. The points 1—4 correspond to the acids cited in Table I, while the points 5—8 belong to di-*n*-butyl-[6], di-ethyl-[7], di-*p*-tolyl- and di-phenyl phosphoric acid esters, respectively.

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IZVLEČEK

Disociacijska, porazdelitvena in dimerizacijska konstanta nekaterih organofosfornih kislin

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Podani so rezultati določitev disociacijske, dimerizacijske in porazdelitvene konstante dveh fosfinskih kislin in dveh monoestrov fosfonskih kislin. Potrjena je veljavnost Hammettove enačbe in določena konstanta ϱ za organofosforne kisline v 1-molarnem perkloratnem mediju.

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