SOLVOLYSIS OF DIPHENYL AMIDOPHOSPHATES IN AQUEOUS ALCOHOLIC MEDIA

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Influence of substituent on the reaction rate of the alkali-catalyzed solvolysis of the studied compound set has been followed. The activation entropy has also been determined. The reaction products have been identified, and their concentration ratio has been determined. The reaction selectivity is mostly influenced by sterical effects in the substrate molecule. The results obtained agree with the S_N2 mechanism.

Alkaline hydrolysis of diesters of amidophosphoric acids follows the equation

$$(RO)_2P(O)NHR + OH^- \rightarrow (RO)P(O)ONHR^- + ROH . \qquad (A)$$

According to literature the rate-limiting step of the reaction consists in attack of phosphorus atom in neutral substrate molecule by OH^- ion. This conclusion is based on dependence of the reaction rate constant *vs* pK of the leaving group[1], activation entropy, ϱ^* constant of the Taft equation of the N-substituted derivatives, ϱ constant of the Hammett equation of the O-substituted derivatives, and existence of relatively stable intermediate[2,3]. Out of the criteria given the first four are taken from carboxylate ester hydrolysis, the found relatively stable intermediate (which was also observed with other phosphorus derivatives[4]) represents an evidence based on chemistry of phosphorus. All the criteria used so far agree with the above-given mechanism except for the unexpectedly small value of the Hammett ϱ constant found in studies of substituent effects on the alkaline hydrolysis rate of diphenyl esters of substituted anilidophosphoric acids[2]. This effect can be due to a number of reasons, however, according to the activation entropies, the S_N2 mechanism is maintained in this case, too. Due to this anomaly it seems useful to extend the available experimental material by further derivatives, and use them in a study of substituent effect on the reaction rate of a series of compounds. The substituent effect on the reaction rate was compared with that on the alkaline solvolysis rate of triphenylphosphates the reaction mechanism of which is known[5-7]. Also it is interesting to follow the influence of composition of solvent on ratio of the reaction products, as concentration ratio of lyate ions in a mixture of two protic solvents changes with their concentration and, at constant concentrations, depends on their acid-base properties. From the formal kinetics viewpoint the reaction changes from an isolated one to a parallel one, the both reactions (*i.e.* hydrolysis and alcoholysis) contributing then to the values of activation enthalpy and entropy.

EXPERIMENTAL

Reagents. Triphenyl[8] (*I*), tri-*p*-methylphenyl[8] (*II*) and tri-*p*-chlorophenyl[9] phosphates (*III*), diphenyl[10] (*IV*), di-*p*-methylphenyl[11] (*V*) and di-*p*-chlorophenyl[11] amidophosphates (*VI*) were prepared according to the literature. Di-*p*-methoxyphenyl (*VII*), di-*m*-methoxyphenyl (*VIII*) and di-*m*-methylphenyl (*IX*) amidophosphates were prepared by ammonolysis of the corresponding ester-chlorides in inert solvent[9]. In similar way the substituted diphenyl esters of morpholidophosphoric acid were prepared, too. Diphenyl morpholidophosphate (*X*) was prepared according to ref.[12]. Di-*p*-methoxyphenyl (*XI*), di-*p*-methylphenyl (*XII*), di-*p*-chlorophenyl (*XIII*) and di-*m*-nitrophenyl (*XIV*) morpholidophosphates were prepared by morpholinolysis of the corresponding ester-chlorides in inert solvent[9]. Diphenyl N-(*m*-nitrophenyl)amidophosphate (*XV*) was prepared according to ref.[13], and diphenyl N-*p*-acetylanilidophosphate (*XVI*) was prepared by the general method[9]. Elemental analyses and melting points of the new substances are given in Table I. Diphenyl N-methylamido- (*XVII*), N-cyclohexylamido- (*XVIII*), N-phenyl-

TABLE I

The Compounds Synthetized

Compound	M.p., °C (solvent)	Formula (m.w.)	Calculated/Found			
			% C	% H	% N	% P
VII	178 (ethanol)	$C_{14}H_{16}NO_5P$ (309·2)	54·38 54·13	5·22 5·32	4·53 4·49	10·02 9·77
VIII	65—67 (ethanol)	$C_{14}H_{16}NO_5P$ (309·2)	54·38 54·35	5·22 5·65	4·53 4·30	10·02 10·00
IX	78—79 (ethanol)	$C_{14}H_{16}NO_3P$ (277·2)	60·65 60·42	5·82 6·07	5·05 4·74	11·17 10·96
XI	87—88 (ethanol))	$C_{18}H_{22}NO_6P$ (379·3)	57·00 56·56	5·85 6·34	3·69 3·67	8·17 8·07
XII	62—64 (ether–pentane)	$C_{18}H_{22}NO_4P$ (348·3)	62·07 61·86	6·37 6·41	4·02 3·90	8·89 8·75
XIII	78—79 (ethanol	$C_{16}H_{16}Cl_2NO_4P$ (388·2)	49·51 49·17	4·15 3·96	3·61 3·59	7·98 7·91
XIV	124—127 (aceton)	$C_{16}H_{16}N_3O_8P$ (409·2)	46·96 47·22	3·94 3·95	10·27 10·47	7·57 7·39
XVI	154—155 (ethanol)	$C_{20}H_{18}NO_4P$ (367·3)	65·40 65·77	4·94 5·10	3·81 3·57	8·43 8·27

amido- (*XIX*) and N-benzylamidophosphates (*XX*) were described in the previous communication[2]. Diphenyl N-dimethylamidophosphate (*XXI*) was prepared according to ref.[14], di-*m*-nitrophenyl (*XXII*) and di-*p*-methoxyphenyl (*XXIII*) N-methylamidophosphates were described in our previous communication[3]. For chromatographical identification of the solvolysis products we used the sodium salts of phenyl, methyl or ethyl esters of substituted amidophosphoric acid described elsewhere[15].

Methods. The dissociation constant was determined photometrically by the standard method[16]. For *XVI* it was found $pK = 11 \cdot 26 \pm 0 \cdot 05$ (λ 346 nm, 50% ethanol by wt.). The reaction kinetics was followed photometrically in glycinate buffers by the method given earlier[2]. The wavelengths used are given in the Tables. The rate constants were calculated from the relation $\log (E_\infty - E) = -(kt/2 \cdot 303) + \text{const.}$ by the least squares method and are loaded with an error lower than 5%. The solvolysis activation parameters were calculated from the rate constants found at 50, 45, 40, 35, 30°C (for the compounds *I* to *III*) and 40, 35, 30, 25, 20°C (for the compounds *IV* to *IX*) using the least squares method. The experiments were carried out in water–alcohol mixed solvents. The autoprotolysis constant K_s and the lyate ion concentration ratio are known[17–19] for the water–methanol system, whereas for water–ethanol no data are available from which the lyate ion concentration ratio could be calculated with sufficient accuracy.

If the solvolysis is first order in lyate ion activity, then the reaction rate obeys Eq. (*1*) in which $a(\text{HA})$, k_1 and k_2 mean the non-ionized substrate activity, the rate constants of parallel hydrolysis and alcoholysis, respectively. Eq. (*1*) can be transformed into (*2*) in which R stands for the lyate ion activity ratio ($R = a(\text{RO}^-)/a(\text{OH}^-)$). Eq. (*2*) is simplified according to Eq. (*3*).

$$v = [k_1 \, . \, a(\text{OH}^-) + k_2 \, . \, a(\text{RO}^-)] \, a(\text{HA}) \tag{1}$$

$$v = [k_1 + k_2 \, . \, R] \, a(\text{OH}^-) \, . \, a(\text{HA}) \tag{2}$$

$$k' = (k_1 + k_2 R) \, a(\text{OH}^-) = k_0 \, . \, a(\text{OH}^-) \tag{3}$$

If the substrate is dissociated, then activity of the non-ionized particles in Eq. (*2*) can be expressed by Eq. (*4*) which is introduced into (*2*) to give (with respect to Eq. (*3*)) Eq. (*5*), and the experimental rate constant is given by Eq. (*6*).

$$a(\text{HA}) = a(\text{H}^+) \, . \, c_\text{T}/[K + a(\text{H}^+)] \tag{4}$$

$$v = k_0 \, . \, a(\text{OH}^-) \, . \, a(\text{H}^+) \, . \, c_\text{T}/[K + a(\text{H}^+)] \tag{5}$$

$$k_\text{exp} = k' \, . \, a(\text{H}^+)/[K + a(\text{H}^+)] \tag{6}$$

In these equations K and c_T mean the dissociation constant of diester of amidophosphoric acid and its overall concentration (sum of its ionized and non-ionized forms), respectively.

In the given solvent the equilibrium (*B*) is established with the equilibrium constant K_i defined by Eq. (*7*). The reaction selectivity was calculated from the relation[20] (*8*) in which $c(\text{XOR})$ and $c(\text{XOH})$ are concentrations of the alcoholysis and hydrolysis products, respectively. The difference between concentration and activity in Eqs (*7*) and (*8*), resp. in Eqs (*1*) to (*3*) were neglected in calculations.

$$\text{OH}^- + \text{ROH} = \text{H}_2\text{O} + \text{RO}^- \tag{B}$$

$$K_i = c(\text{RO}^-) \, . \, c(\text{H}_2\text{O})/c(\text{OH}^-) \, . \, c(\text{ROH}) \tag{7}$$

$$S = \log [c(\text{XOR})/c(\text{XOH})] - \log [c(\text{RO}^-)/c(\text{OH}^-)] \tag{8}$$

For identification of the reaction products the substrate was solvolyzed at the temperatures identical with those of kinetic experiments in 0·1M-NaOH solutions. The substrate concentration was 0·05M in both water–methanol and water–ethanol mixtures. After finished solvolysis the solution was analyzed chromatographically and amount of the products was determined quantitatively by the method given earlier[3] with accuracy ± 1%.

RESULTS AND DISCUSSION

For comparison of substituent effects in a reaction which is applied to several groups of compounds it is always necessary to know the reaction mechanism. The model compounds group chosen for diphenyl amidophosphates were the triphenyl phosphates whose hydrolysis to the 1. degree proceeds as an attack of phosphorus atom by OH^- ion in the rate-limiting step[5-7]. The intermediate formed is stabilized by splitting of P—O bond in case of aryl esters[21,22], whereas C—O bond is split with trialkyl esters[23,24]. The dependence $\log K$ *vs* pH found in this work (Table II) for *I* to *III* confirms that the reaction is 1. order in OH^- activity. The activation parameters of the compound *I* in 0·01M-NaOH ($\Delta H^{\ddagger} = 52{\cdot}7\ \text{kJ mol}^{-1}$, $\Delta S^{\ddagger} = -94{\cdot}7\ \text{J mol}^{-1}\ \text{K}^{-1}$) and positive sign of the Hammett ϱ constant ($\varrho = 4{\cdot}0$ at pH 12·08 at 30°C) confirm bimolecular character of the rate-limiting step in accordance with refs[25,26].

With respect to discussion of the reaction mechanism of diphenyl amidophosphates the most simple are those compounds which have the both NH_2 hydrogen atoms substituted by alkyl groups being thus unable of dissociation, *i.e.* *X* to *XIV*. According to the dependence $\log k_{exp}$ *vs* pH the alkaline hydrolysis of *X* is 1. order

TABLE II

Hydrolysis Rate Constants ($k_{exp} \cdot 10^5$, s^{-1}) of Substituted Triphenyl Phosphates in 50% (by wt.) Ethanol at 30°C at the Given pH and Wavelength

pH	*I* (236·5 nm)	*II* (239 nm)	*III* (246 nm)
10·41	—	—	1·72
10·53	—	—	1·85
11·11	0·351	—	6·36
11·46	0·706	—	11·19
11·73	1·43	—	17·46
12·08	2·67	0·785	28·21
12·47	6·96	1·45[a]	—
12·68	12·79	3·89	—
12·86	21·29	7·09	—

[a] At pH 12·31.

in OH^- ion[2]. The activation entropy found indicates undoubtedly the S_N2 mechanism of the rate-limiting step[2]. Dependence of the rate constants on substitution of the aromatic ring (in *X* to *XIV*) also agrees with this mechanism. At 90°C at pH 12·71 the following rate constants were found in 50% (by wt.) aqueous ethanol:

Compound (λ, nm)	*X* (236·5)	*XI* (238)	*XII* (239)	*XIII* (246)	*XIV* (227·5)
$k_{exp} \cdot 10^5$, s^{-1}	8·09	4·77	4·13	53·8	708

The rate constant of *XIV* was obtained by extrapolation log *k* *vs* pH from the values obtained at lower pH where the reaction was easier measurable. The following data were used for the extrapolation:

pH	10·19	10·33	10·43	10,81	11·32
$k_{exp} \cdot 10^5$, s^{-1}	3·21	3·86	5·37	10·2	38·0

Except for *XI* the dependence log k_{exp} *vs* substituent constants complies with the Hammett equation with $\varrho = 2·53$ which stands in good accordance with the ϱ constant values of solvolysis of substituted diphenyl N-methylamidophosphates ($\varrho = 2·47$ at pH 11·91 at 45°C) and anilidophosphates ($\varrho = 3·01$ at pH 11·62 at 45°C) in the same medium[3]. Numerical value of the ϱ constant is, of course, lower than that of the same reaction of substituted triphenyl phosphates and confirms the above-mentioned ideas[2,3] according to which the reaction consists in interaction of non-ionized diphenyl N-methylamido- and anilidophosphates with lyate ions. The σ constant values used in the present work were taken from ref.[27].

Furthermore the pH dependence of the solvolysis rate constants of substituted diphenyl amidophosphates was followed in 50% (by wt.) ethanol at 20°C (Table III). In all the cases (*IV* to *IX*) slope of the dependence log k_{exp} *vs* pH was practically unity, which indicates that the solvolysis of these compounds is 1. order in the lyate ion activity. Therefore, constant k_0 can be calculated from the pH measured and Eq. (*3*), and its temperature dependence was used for calculation of the activation parameters. The following values were obtained for 25°C:

Compound	*IV*	*V*	*VI*	*VII*	*VIII*	*IXX*
$\Delta H^{\ddagger}$, kJ mol^{-1}	47·3	53·5	55·1	59·7	59·1	56·3
$-\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	68·4	71·6	47·9	50·3	45·5	63·2

The found results prove (in accordance with ref.[25]) the bimolecular character of the rate-limiting step. The $\Delta S^{\ddagger}$ value for *IV* and the reaction order in the lyate ions given in the present paper are considered more precise than those published earlier[2].

With respect to the previous communication[2] it can be judged that pK values of these compounds are above 14, and, hence, amount of the non-ionized form is negligible at the pH used. Therefore, the measured rate constant were used without further corrections for calculation of ϱ constant. The rate constants measured at pH 11·18 complied (with exception of *VII*) with the Hammett equation with $\varrho = 1{\cdot}85$. Positive sign of the ϱ constant again agrees with the idea of bimolecular mechanism of the rate-limiting step. From the given facts it can be concluded that substituents in the aromatic ring bound to phosphorus through oxygen results in positive value of the ϱ constant, whereas substituents in the benzene ring bound to phosphorus through nitrogen atom (in diesters of anilidophosphoric acid) do not practically affect the reaction rate. This finding does not contradict the proposed reaction mechanism, as in some cases the observed ϱ constant value was practically zero even in S_N2 reactions at carbon atom[28].

The rate constants k_{exp} found in solvolyses of *XV* and *XVI* are partly pH-dependent and partly pH-independent (Fig. 1). For *XVI* the both linear parts intersect at pH 11·2 which is close to pK of this compound. Hence, solvolysis of *XVI* proceeds in the region of its pK, and the dependence log k_{exp} *vs* pH is complicated by dissociation of the compound, one of its forms only undergoing the reaction. Let us presume this form to be the neutral molecule *XVI* adding lyate ion at phosphorus atom in the rate-limiting step. This presumption agrees with literature[29], as the addition of lyate ion to neutral derivatives of phosphoric acid is more advantageous thermodynamically than that of the solvolytic reagent to its anion. In solutions with $a(\mathrm{H})^+) \gg K$, K can be neglected as compared with $a(H)^+$ (Eq. (5)), and the experimentally found rate

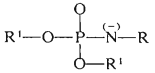
TABLE III

Hydrolysis Rate Constants of Substituted Diphenyl Amidophosphates in 50% (by wt.) Ethanol at 20°C at the Given pH and Wavelength (nm)

pH	*IV* (236·5)	*V* (239·0)	*VI* (246·0)	*VII* (238·0)	*VIII* (239·5)	*IX* (240·5)
9·92	—	—	2·05	—	—	—
10·30	1·16	—	5·54	—	—	—
10·62	2·30	0·91	9·28	0·85	2·60	1·05
11·18	9·46	5·09	27·62	5·18	10·98	5·61
11·41	15·27	—	—	—	—	—
11·54	21·32	13·11	61·27	14·50	30·91	13·84
11·75	30·79	17·22	—	18·81	40·05	19·07
12·12	71·34	38·69	—	43·54	—	46·67
12·20	—	45·16	—	50·87	—	51·68

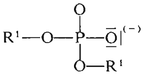
constant increases linearly with increasing activity of lyate ions. If $a(H^+) \ll K$, then $a(\mathrm{H}^+)$ can be neglected, and the k_{exp} found is practically pH-independent. According to Eq. (*3*) $\log k'$ increases linearly with pH, slope of this dependence being close to unity (Fig. 1). This fact confirms the above-mentioned presumption that the neutral molecule *XVI* is the reactive form.

The alternative hypothetical hydrolysis mechanism of diphenyl amidophosphates consisting in slow splitting off of phenoxide anion from A_1 to give plane intermediate with trivalent phosphorus ($\mathrm{R^1{-}O{-}P(O){=}N{-}R^2}$) and subsequent fast addition of solvent[30] by ElcB mechanism seems to be excluded by comparison with hydrolysis of the anion A_2 following the $\mathrm{S_N}2$ mechanism[7]. The anion A_3 is hydrolyzed with difficulty, too, or its hydrolysis was not observed at all[30–33]. Hence easy splitting off of phenoxide ion from the anion A_1 also cannot be expected, which excludes its solvolysis by ElcB mechanism. Comparison of the found activation entropy with literature data[25] and comparison of reactivities of the anions A_2 and A_3 with that of A_1 confirm the $\mathrm{S_N}2$ mechanism of the solvolysis of diesters of amidophosphoric acids. From the facts given in the present and the previous[1–3] communications it follows that all the approaches used indicate the $\mathrm{S_N}2$ mechanism of the rate-limiting step of the solvolysis of the studied compound set. Uniform mechanism enables orientation in selectivity of this reaction to lyate ions.



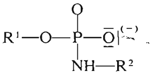
$$\mathrm{R^1{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O{-}R^1}{P}}{-}\overset{(-)}{N}{-}R}$$

A_1



$$\mathrm{R^1{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O{-}R^1}{P}}{-}\overline{O}|^{(-)}}$$

A_2



$$\mathrm{R^1{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle NH{-}R^2}{P}}{-}\overline{O}|^{(-)}}$$

A_3

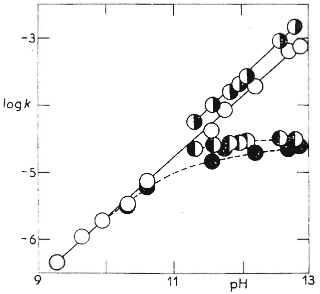
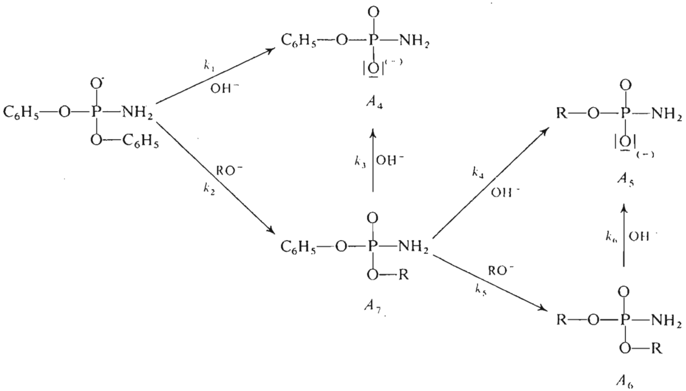


Fig. 1

Hydrolysis Rate Constants of Diphenyl N-(*m*-Nitrophenyl)-amidophosphate (◐ k_{exp}, ◑ k') and Diphenyl *p*-Acetylanilidophosphate (● k_{exp}, ○ k') in 50% (by wt.) Ethanol at 46°C

The compound *IV* was solvolyzed in 90% (by wt.) methanol and in 92·8% (by wt.) ethanol at 25°C. Mole fraction of alcohol is the same (0·835) in the both solvents. Chromatographical identification with standards showed that in these solvents the solvolysis follows the formalism of parallel reactions. According to the chromatography the reaction mixture contained A_4, A_5 and A_6. The mixed ester A_7 could not be trapped, but it can be presumed with respect to the safely identified A_6 and A_5. Scheme 1 can be written for the solvolysis.



SCHEME 1

In this Scheme k_3 must be much lower than k_4 and k_5 for the phenoxide ion to be better leaving group than alkoxide ions[34,35], and thus this reaction can be neglected as kinetically insignificant. The hydrolysis product A_4 undergoes further solvolysis under much more vigorous conditions[31], A_5 undergoes no further solvolysis at all[33]. By withdrawing samples at regular time intervals and their chromatographical analysis it was proved that, under the given conditions, A_6 is solvolyzed very slowly, and, hence, the concentration ratio of A_4, A_5 and A_6 remains constant for a long period. Average value of this concentration ratio from five analyses was $A_4 : A_5 : A_6 = 4·2 : 4·2 : 91·6$ and 39·4; 23·0 : 37·6 in aqueous methanol and aqueous ethanol, respectively. Ratio of methanolysis and hydrolysis products of *IV* is 22·8, and for A_7 it is 21·8. Ratio of ethanolysis and hydrolysis products of *IV* is 1·54, and for A_7 it is 1·64. Ratio of the hydrolysis and alkoholysis rates in a given water–alcohol pair is the same for *IV* and A_7 within experimental error. It differs for solutions of different alcohols at a given molar fraction. For varying composition water–methanol the alkali solvolysis of *IV* gave the following concentration ratios of reaction products, wherefrom the reaction selectivity was calculated using the data[18]:

Wt.% CH_3OH	20	28·5	41	50	60	70	80	90
$c(XOR)/c(XOH)$	1·051	1·668	2·755	3·67	5·62	6·81	11·65	22·8
Selectivity	0·611	0·598	0·596	0·539	0·548	0·501	0·409	0·252

The selectivity is somewhat changed with changing solvent composition. Undoubtedly this is also due to dependence of the constant K_i (Eq. (7)) on the solvent composition.

A marked change of solvolysis can be achieved by sterical changes. The reaction selectivity remains practically unchanged on substitution of hydrogen in $—NH_2$ by methyl group (*cf.* the data for *IV* and *XVII* in Table IV), but it changes markedly by substitution of hydrogen by phenyl (*XVIII*) or cyclohexyl group (*XIX*). Further marked selectivity change can be brought about by substitution of the both hydrogen atoms by alkyl groups (*cf. X* and *XXI*). It is obvious that acid-base properties of the substrate and, hence, a possible contribution of the ElcB mechanism have little effect on the reaction selectivity. This fact was verified by substitution in the phenol ring, the following product concentration ratios being obtained in 50% (by wt.) ethanol at 20°C:

Compound	*XVII*	*XXII*	*XXIII*
$c(XOR)/c(XOH)$	0·228	0·297	0·297

TABLE IV

Product Concentration Ratio $c(XOR)/c(XOH)$ of the Solvolysis Studied and Its Selectivity in Water–Alcohol System

Alcohol percentage (by wt.)	*IV*	*XVII*	*XVIII*	*XIX*	*XX*	*XXI*	*X*
41% CH_3OH $c(XOR)/c(XOH)$	2·76	2·63	1·11	1·34	1·70	0·12	0·40
selectivity	0·596	0·575	0·200	0·282	0·385	−0·766	−0·243
50% C_2H_5OH $c(XOR)/c(XOH)$	0·23	0·23	0·075	0·032	0·107	—	—

For the compound *XVII* the temperature dependence of ratio of product concentrations of the parallel reactions in 50% (by wt.) ethanol was also investigated, and the following values were obtained:

Temperature, °C	20	45	70
$c(XOR)/c(XOH)$	0·228	0·214	0·163

Reactivity of nucleophile depends on both its basicity and polarizability[36], being almost the same for the neutral molecules of methanol and ethanol in reactions without sterical effects; in sterically hindered reactions less bulky nucleophiles are more favoured (H_2O *vs* C_2H_5OH; OH^- *vs* $C_2H_5O^-$) (ref.[37-39]). If the alcohol molecule is the nucleophile, then the product ratio of the reesterification reactions differs but little in the mixtures water–methanol and water–ethanol[40]. Differences in order of magnitude between concentration ratios of the reaction products in mixtures water–methanol and water–ethanol confirm thus the idea of the lyate ion being the nucleophile (not the solvent molecule). This fact along with that one that slope of the dependence log k *vs* pH equals unity again confirm the idea of attack of the neutral substrate molecule by lyate ion. Marked influence of sterical effects contributes to this conclusion. Therefore, it can be concluded that comparison of reactivity of diphenyl amidophosphates with that of other esters of phosphoric acid and analysis of the reaction products agree in confirming the previous conclusion about S_N2 mechanism of the studied reaction which proceeds by a slow attack of the substrate molecule by lyate ion and subsequent rapid elimination of phenoxide ion.

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