

ALKALINE SOLVOLYSIS OF DIAMIDOPHOSPHATES

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Mechanism of alkaline solvolysis of phenyl diamidophosphates is discussed on the basis of its selectivity, activation entropy and steric effects. All methods used show that the reaction proceeds by S_N2 mechanism *via* an intermediate, containing a pentavalent phosphorus.

Solvolytic reactions have been often studied with regard to the electrophile whereas studies concerning the solvent (which is usually a nucleophile) are only scarce. Thus, study of selectivity of solvolysis in a mixed solvent, composed of two prototropic components may contribute to mechanism elucidation: it can reveal reactivity of the intermediate and for reactions of some compounds in alkaline media it can also decide whether the nucleophile is represented by the solvent molecule or its lyate ion. This extends our knowledge of reaction intermediates; because of small number of analogous data it seems reasonable to correlate the results of the selectivity studies with methods based on reactivity of carboxylic acids esters.

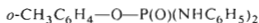
Alkaline hydrolysis of triesters and diesters of phosphoric acid¹, as well as of diesters of amidophosphoric acids, proceeds by S_N2 mechanism²⁻⁷. On the other hand, an $E1cB$ mechanism is ascribed^{8,9} to the rate-determining step in alkaline hydrolysis of diamidophosphates. Monomolecular mechanism is also assumed for solvolysis of monoaryl esters of mono- and dianion of phosphoric acid^{10,11}; this assumption was confirmed by non-selective reesterification in aqueous methanol. The aim of the present work is to verify the validity of the reaction mechanism, suggested for alkaline solvolysis of diamidophosphates^{8,9}.

EXPERIMENTAL

Chemicals. Phenyl diamidophosphates were prepared by aminolysis of dichlorides of substituted phenyl phosphates in an inert solvent. Preparation of derivatives of weakly basic amines was catalyzed with pyridine¹². Following compounds were prepared: phenyl¹³ (*Ia*), *p*-methoxyphenyl (*Ib*), *p*-tolyl (*Ic*), *m*-tolyl (*Id*) and *p*-chlorophenyl (*Ie*) diamidophosphate; phenyl¹⁴ (*IIa*), *p*-tolyl (*IIb*), *m*-tolyl (*IIc*), *p*-methoxyphenyl (*IId*), *m*-methoxyphenyl (*IIe*), *p*-chlorophenyl (*IIf*) and *m*-nitrophenyl (*IIg*) N,N' -dimethyldiamidophosphate; phenyl N,N' -dibenzoyldiamidophosphate¹⁵ (*IIIa*) and phenyl N,N' -dicyclohexyldiamidophosphate¹⁴ (*IIIb*). Further, we prepared phenyl dianilido-¹⁴ (*IIIc*), di(*p*-methylanilido)-¹⁶ (*IIId*), di(*p*-methoxyanilido)- (*IIIe*), di(*m*-chloro-

anilido)- (*III*f), di(*p*-bromoanilido)- (*III*g), di(*p*-acetalanilido)- (*III*h), di(*m*-nitroanilido)- (*III*i) and di(*p*-dimethylaminoanilido)phosphate (*III*j). For chromatographic identification of solvolysis products we prepared methyl and ethyl¹⁷ di(*N*-methylamido)phosphate (*III*h and *III*i, respectively) by aminolysis of phosphoric acid monoester dichloride. The compound *III*i was not isolated in the pure state. We prepared also sodium di(*N*-methylamido)phosphate¹⁸ (*II*j). Finally, *o*-tolyl diamidophosphate (*I*f), di(*N*-methylamido)phosphate (*II*k) and dianilidophosphate (*IV*) were prepared. The analytical data for the newly prepared compounds, together with their melting points, are given in Table I.

$R-O-P(O)(NH_2)_2$	$R-O-P(O)(NHCH_3)_2$	$C_6H_5-O-P(O)(NHR)_2$
<i>Ia</i> , R = C ₆ H ₅	<i>IIa</i> , R = C ₆ H ₅	<i>IIIa</i> , R = C ₆ H ₅ CH ₂
<i>Ib</i> , R = <i>p</i> -CH ₃ OC ₆ H ₄	<i>IIb</i> , R = <i>p</i> -CH ₃ C ₆ H ₄	<i>IIIb</i> , R = C ₆ H ₁₁
<i>Ic</i> , R = <i>p</i> -CH ₃ C ₆ H ₄	<i>IIc</i> , R = <i>m</i> -CH ₃ C ₆ H ₄	<i>IIIc</i> , R = C ₆ H ₅
<i>Id</i> , R = <i>m</i> -CH ₃ C ₆ H ₄	<i>IId</i> , R = <i>p</i> -CH ₃ OC ₆ H ₄	<i>IIId</i> , R = <i>p</i> -CH ₃ C ₆ H ₄
<i>Ie</i> , R = <i>p</i> -ClC ₆ H ₄	<i>IIe</i> , R = <i>m</i> -CH ₃ OC ₆ H ₄	<i>IIIe</i> , R = <i>p</i> -CH ₃ OC ₆ H ₄
<i>If</i> , R = <i>o</i> -CH ₃ C ₆ H ₄	<i>IIf</i> , R = <i>p</i> -ClC ₆ H ₄	<i>IIIf</i> , R = <i>m</i> -ClC ₆ H ₄
	<i>IIg</i> , R = <i>m</i> -NO ₂ C ₆ H ₄	<i>IIIg</i> , R = <i>p</i> -BrC ₆ H ₄
	<i>IIIh</i> , R = C ₂ H ₅	<i>IIIh</i> , R = <i>p</i> -CH ₃ COC ₆ H ₄
	<i>IIIi</i> , R = CH ₃	<i>IIIi</i> , R = <i>m</i> -NO ₂ C ₆ H ₄
	<i>IIIk</i> , R = <i>o</i> -CH ₃ C ₆ H ₄	<i>IIIj</i> , R = <i>p</i> -(CH ₃) ₂ NC ₆ H ₄



IV

Methods. The pH measurement procedure has already been described¹⁹. For the p*K* measurements 2 to 8 · 10⁻⁵ mol dm⁻³ solutions of the compounds in 50% (wt) ethanol were prepared; these were mixed with the same volume of a glycinate buffer in the same solvent. Spectra of the ionized and non-ionized forms were measured on a Specord UV VIS (Zeiss, Jena) spectrophotometer in 1 cm quartz cells and, according to the spectra, wavelength suitable for the measurement and calculation of p*K* was selected. At this wavelength absorbances of the solutions at various pH were determined at room temperature. These data, together with the measured pH values of the solutions, served for calculation of the acid-base dissociation constants from the equation²⁰ $E = (a_{H^+}/K)(E_A - E) + E_B$, where *K* is the dissociation constant, *E_A* absorbance of solution of the non-ionized form, *E_B* absorbance of solution of the anion, and *E* absorbance of solution, containing the ionized as well as non-ionized form of the compound at the given activity of hydrogen ions, *a_{H+}*.

Kinetic measurements were carried out using the previously described⁴ method. The rate constants were calculated from the equation $\log(E_\infty - E) = -(kt/2.303) + \text{const}$ by the least squares method with error less than 5%. The ampoule technique was used for compounds *IIa* to *IIg* and *IIIa-IIIj*. Activation parameters were calculated from five rate constants, determined at 20, 25, 30, 35 and 40°C (compounds *Ia-Ie*) or from four values determined at 60, 70, 80 and 90°C (*IIa-IIg*, *IIIa-IIIj*).

The solvolysis of *IIf* (0.05 mol/dm³) in water-alcohol mixtures was performed at room temperature in 0.1 mol/dm³ sodium hydroxide solutions. Samples for analysis of the solvolysis products were taken after 5 min; after this time chromatographic analysis (performed as described⁶ previously) detected no starting compound in the reaction mixture.

TABLE I
New compounds

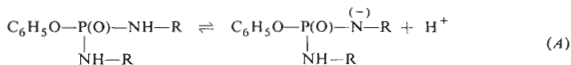
Compound	M.p., °C (solvent)	Formula (mol.wt.)	Calculated/Found			
			% C	% H	% N	% P
<i>Ib</i>	172 (dec.) (ethanol)	$C_7H_{11}N_2O_3P$ (202.1)	41.59 42.11	5.49 5.67	13.86 13.36	15.32 15.78
<i>Ic</i>	178—181 (dec.) (ethanol)	$C_7H_{11}N_2O_2P$ (186.1)	45.17 45.04	5.96 6.28	15.05 14.81	16.64 16.81
<i>Id</i>	104 (ethanol)	$C_7H_{11}N_2O_2P$ (186.1)	45.17 44.54	5.96 6.32	15.05 15.31	16.64 16.49
<i>Ie</i>	157 (dec.) (ethanol)	$C_6H_8ClN_2O_2P$ (206.6)	34.89 34.90	3.90 4.19	13.56 13.59	15.00 15.02
<i>If</i>	149—51 (ethanol)	$C_7H_{11}N_2O_2P$ (186.1)	45.17 45.07	5.96 6.10	15.05 15.56	16.64 16.57
<i>IIb</i>	91 (ethanol-water)	$C_9H_{15}N_2O_2P$ (214.2)	50.47 50.08	7.06 7.04	13.08 12.88	14.46 14.46
<i>IIc</i>	80—82 (ethanol)	$C_9H_{15}N_2O_2P$ (214.2)	50.47 50.53	7.06 7.12	13.08 12.88	14.46 15.26
<i>IId</i>	104 (ethanol)	$C_9H_{15}N_2O_3P$ (230.2)	46.96 47.16	6.57 6.63	12.17 12.03	13.46 13.63
<i>IIe</i>	53—54 (ether- CCl_4)	$C_9H_{15}N_2O_3P$ (230.2)	46.96 47.15	6.57 6.48	12.77 11.96	13.46 13.85
<i>IIf</i>	67—69 (ethanol-water)	$C_8H_{12}ClN_2O_2P$ (234.6)	40.96 41.88	5.16 4.99	11.94 11.69	13.20 13.34
<i>IIg</i>	115—116 (ethanol)	$C_8H_{12}N_3O_4P$ (245.2)	39.20 39.42	4.93 4.95	17.14 16.98	12.63 12.64
<i>IIIk</i>	104 (ethanol)	$C_9H_{15}N_2O_2P$ (214.2)	50.47 50.25	7.06 7.06	13.08 13.37	14.46 14.29
<i>IIIe</i>	149—151 (ethanol)	$C_{20}H_{21}N_2O_4P$ (384.3)	62.50 62.48	5.51 5.52	7.29 7.16	8.06 8.47
<i>IIIf</i>	111—112 (ethanol)	$C_{18}H_{15}Cl_2N_2O_2P$ (393.2)	54.99 55.01	3.85 3.96	7.12 6.77	7.88 7.89
<i>IIIg</i>	208—210 (ethanol)	$C_{18}H_{15}Br_2N_2O_2P$ (482.1)	44.84 44.89	3.14 3.17	5.81 5.63	6.43 6.58
<i>IIIh</i>	243—244 (acetone)	$C_{22}H_{21}N_2O_4P$ (408.4)	64.71 64.88	5.18 5.33	6.86 6.63	7.58 7.58
<i>IIIi</i>	202—203 (ethanol)	$C_{18}H_{15}N_4O_6P$ (414.3)	52.19 52.05	3.65 3.77	13.52 13.20	7.48 7.38

TABLE I
(Continued)

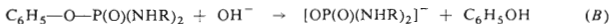
Compound	M.p., °C (solvent)	Formula (mol.wt.)	Calculated/Found			
			% C	% H	% N	% P
IIIj	82–84 (ethanol)	C ₂₂ H ₂₇ N ₄ O ₂ P (410.4)	64.38	6.63	13.65	7.55
			63.64	6.70	13.70	7.47
IV	135 (ether)	C ₁₉ H ₁₉ N ₂ O ₂ P (338.3)	67.45	5.66	8.28	9.16
			66.99	5.62	8.29	9.17

RESULTS AND DISCUSSION

Alkaline solvolysis. As shown by the spectral data, in alkaline solutions compounds IIIj–IIIi are markedly dissociated. The dissociation constants found for the acid–base equilibrium (equation (A)) are given in Table II. Aryl esters of other compounds studied had pK values greater than 14.



Alkaline hydrolysis of the studied group of compounds splits off phenol, affording diamidophosphates⁸ as described by equation B.



Rate constants of this reaction depend on the pH of the solution, as seen from Tables III, IV and V. For compounds Ia–If, IIa–IIg, IIk, IIIa–IIIe, IIIj and IV whose pK values are at least one unit larger than pH values of the studied solutions, we found a linear dependence of $\log k_{\text{exp}}$ on pH, whose slope was approximately unity. For compounds IIIf–IIIi this dependence was influenced by dissociation. When k_{exp} were transformed into rate constants for the non-ionized form⁴ using the equation $k_{\text{exp}} = k' \cdot a_{\text{H}^+} / (K + a_{\text{H}^+})$, linear dependence of k' on pH with unit slope was also found, similar to dependences described in the literature⁶. It is thus obvious that the solvolytic reaction is of the first order relative to activity of the lyate ions for all the studied compounds.

Solvolysis of compound IIIh could be followed in a sufficiently broad range of pH; at a sufficiently low pH we observed an induction period which, similarly

to other cases, corresponded to formation of a relatively stable intermediate^{4,5,21}. Such an intermediate can be only a pentavalent phosphorus derivative because it is much more stable than the hypothetical imino derivative containing a trivalent phosphorus atom²². The mentioned experiment is consistent with an S_N2 reaction mechanism whereas it cannot fit the suggested E1cB mechanism^{8,9}.

Activation entropy. Compounds *Ia–Ie* reacted too rapidly to allow experimental determination of the corresponding second-order rate constants. Their rate constants were therefore measured in buffers of pH 11.32. The thus-obtained rate constants depend on the lyate ions activity L⁻ ($k_{\text{exp}} = k \cdot a_{\text{L}^-}$) which can be calculated from the measured pH and from the solvent autoprotolysis constant (on interpolation,

TABLE II

Dissociation constants of aryl anilidophosphates at room temperature in 50% (wt) ethanol (determined at the wavelengths given)

Compound (λ nm)	<i>III</i> f (261)	<i>III</i> g (263)	<i>III</i> h (346)	<i>III</i> i (255.5)
pK	13.09	13.67	11.68	11.34

TABLE III

Rate constants, $k_{\text{exp}} \cdot 10^4$ (s⁻¹), of solvolysis of substituted phenyl diamidophosphates in 50% (wt) ethanol at 20°C at the given pH (determined by the wavelengths given)

pH	<i>Ia</i> (236.5 nm)	<i>Ib</i> (238 nm)	<i>Ic</i> (239 nm)	<i>Id</i> (240.5 nm)	<i>Ie</i> (246 nm)
10.19	—	—	—	—	0.642
10.32	0.370	—	—	—	—
10.43	—	—	—	—	1.02
10.58	0.747	—	—	—	—
10.75	1.31	—	—	—	—
11.04	2.32	1.88	—	2.53	—
11.13	2.95	—	—	—	—
11.32	—	4.50	4.97	5.35	13.3
11.41	5.87	—	—	—	—
11.59	—	12.4	8.58	12.4	23.7
11.83	—	16.3	14.1	20.7	—
11.97	—	—	19.5	—	—

TABLE IV

Rate constants, $k_{\text{exp}} \text{ m } 10^4 \text{ (s}^{-1}\text{)}$, of solvolysis of substituted phenyl $\text{N,N}'\text{-dialkyl}(\text{diamidophosphates in } 50\% \text{ (wt) ethanol at } 70^\circ\text{C and given pH}$
(followed at the given wavelength, nm)

pH	<i>Ila</i> (236.5)	<i>Iib</i> (239)	<i>Iic</i> (240.5)	<i>Iid</i> (238)	<i>Iie</i> (239.5)	<i>Iif</i> (246)	<i>Iig</i> (230)	<i>Iiha</i> (236.5)	<i>Iiib</i> (236.5)
9.98	—	—	—	—	—	—	0.173	—	—
10.32	—	—	—	—	—	0.134	0.460	—	—
10.75	—	—	—	—	—	0.240	1.460	—	—
11.06	0.187	—	—	—	0.186	0.502	2.66	0.193	—
11.32	—	—	—	—	—	0.817	4.50	—	—
11.41	—	0.168	0.210	0.112	0.317	—	—	—	—
11.49	0.295	—	—	—	—	—	—	0.292	—
11.70	0.527	—	—	—	—	—	—	0.653	—
11.78	—	0.285	0.387	0.252	0.843	—	—	—	—
11.81	—	—	—	—	—	1.98	—	—	—
11.91	0.805	—	—	—	—	—	—	0.772	—
12.05	—	0.672	0.692	0.525	1.42	—	—	—	—
12.10	1.13	—	—	—	—	3.76	—	1.04	0.028
12.30	2.48	—	—	—	—	—	—	2.50	—
12.34	—	0.985	1.36	1.04	3.11	—	—	—	0.056
12.60	5.63	—	—	—	—	—	—	—	—
12.85	—	5.37	7.21	4.61	—	—	—	—	—
12.89	—	—	—	—	—	—	—	—	0.297

TABLE V

Rate constants, $k_{\text{exp}} \cdot 10^4$ (s^{-1}) of solvolysis of substituted phenyl diamidophosphates in 50% (wt) ethanol at 70°C and given pH (followed at the given wavelength, nm)

pH	IIIc (287.5)	IIIId (287.5)	IIIe (287.5)	IIIJ (287.5)	IIIg (287.5)	IIIh (346)	IIIi (236.5)	IIIj (287.5)
9.93	—	—	—	—	—	0.051	—	—
10.19	—	—	—	—	—	0.060	—	—
10.43	—	—	—	—	—	0.083	—	—
11.04	—	—	—	—	—	0.404	—	—
11.32	—	—	—	—	—	0.575	—	—
11.59	—	—	—	—	—	0.837	—	—
11.73	—	—	—	0.647	0.589	0.787	2.75	—
11.91	0.235	—	—	—	—	—	—	—
12.08	0.303	0.296	0.193	1.14	1.07	1.10	2.88	0.123
12.31	0.643	0.522	0.342	1.82	1.82	1.17	3.42	0.234
12.60	1.49	—	—	—	—	—	—	—
12.68	—	1.68	0.964	3.20	4.33	1.28	3.33	0.870
12.79	2.73	—	—	—	—	—	—	—
12.86	—	2.82	1.86	4.94	—	1.21	3.17	2.05
13.08	—	6.62	3.80	—	—	—	—	3.58

the published data²³ for 50% (wt) ethanol give $K_s = 1.38 \cdot 10^{-15}$). Thus, from the temperature dependence of first-order rate constants and solvent autoprotolysis constant we can calculate ΔS^\ddagger values, comparable with those published²⁴. The solvolysis rate constants for the remaining compounds were determined in 0.01 mol/dm³ NaOH. The results, given in Table VI, are invariably in the region of values given²⁴ for the S_N2 mechanism and agree also with the activation entropy values found for alkaline hydrolysis of other diamidophosphates⁹.

Hammett equation. If applied to a group of compounds capable of ionisation, the Hammett equation suffers from a subjective factor, since it requires an assumption that the reacting species is either a neutral electrophile molecule or its ion arising by pre-dissociation. Being aware of this risk, let us assume that the solvolysis concerns a neutral molecule according to equation (B). Then, the ρ constant must be

TABLE VI

Activation parameters for alkaline solvolysis of phenyl diamidophosphates in 50% (wt) ethanol at 298.14 K and the given pH

Compound	pH	ΔH^\ddagger , kJ mol ⁻¹	$-\Delta S^\ddagger$, J mol ⁻¹ K ⁻¹
Ia	10.58	54.9	51.9
Ib	11.32	57.8	41.3
Ic	11.32	52.1	58.9
Id	11.32	55.0	49.4
Ie	11.32	49.2	61.4
IIa	12.32	64.4	78.3
IIb	12.32	64.0	86.0
IIc	12.32	65.6	78.4
IId	12.32	67.1	77.1
IIe	12.32	63.3	78.5
IIf	11.32	67.7	57.1
IIg	11.06	72.9	26.8
IIIa	12.30	66.4	69.2
IIIb	12.89	81.0	58.2
IIIc	12.31	74.0	58.6
IIId	12.31	71.5	67.5
IIIe	12.31	80.4	45.8
IIIf	12.31	78.5	35.8
IIIg	12.31	78.5	36.8
IIIh	12.31	76.6	32.9
IIIi	12.31	79.1	10.7
IIIj	12.31	82.3	42.7

calculated from the constants k' , related with k_{exp} as mentioned above. The obtained rate constants for *Ia*–*Ie* at pH 11.59 and 20°C afford $\rho = 1.10$, for *Ila*–*Ilg* at pH 11.78 and 70°C $\rho = 1.90$. The ρ values are lower than those found for substituted diphenyl amidophosphates⁶ ($\rho = 1.85$), N-methylamidophosphates⁵ ($\rho = 2.47$), N-phenylamidophosphates⁵ ($\rho = 3.01$) and morpholidophosphates ($\rho = 2.53$) which again are lower than the values found for substituted triphenyl phosphates⁶ ($\rho = 4.04$). It is obvious that the thus-obtained ρ value for substituted phenyl diamidophosphates, together with other substituted phenyl phosphates, forms a logical sequence and thus justifies the above assumption. The positive sign of ρ value (cf. alkaline hydrolysis of esters²⁵) confirms the S_N2 mechanism of the studied reaction. The reaction mechanism was verified also by use of the Taft equation, the positive ρ^* constant corresponding to an S_N2 mechanism of the given reaction²⁶ (cf. alkaline hydrolysis of esters²⁶). The rate constants for solvolysis of *Ia*, *Ila*, *IIIa* and *IIIb* in 50% (wt) ethanol at pH 12.50 and 70°C (k_{exp} for *Ia* was obtained by extrapolation since the reaction was too fast under the given conditions) gave $\rho^* = +4.1$.

Steric effects. Reactions, proceeding *via* intermediates with tri- or pentavalent phosphorus, can be distinguished by steric effects. Phenyl and *o*-tolyl esters, reacting *via* a planar trivalent phosphorus-containing intermediate have almost the same reaction rate whereas in reactions, involving an intermediate with a pentavalent

TABLE VII

Rate constants for alkaline solvolysis of phenyl and *o*-tolyl diamidophosphates in 50% (wt) ethanol at the given pH and temperature

pH (t °C)	11-13 (20)	12-23 (70)	12-23 (70)
k, s ⁻¹ for	<i>Ia</i> 2.95 · 10 ⁻⁴ <i>If</i> 1.71 · 10 ⁻⁴	<i>Ila</i> 2.09 · 10 ⁻⁴ <i>IIk</i> 1.46 · 10 ⁻⁵	<i>IIIc</i> 5.37 · 10 ⁻⁵ <i>IV</i> 6.91 · 10 ⁻⁶

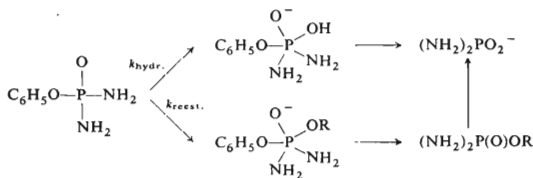
TABLE VIII

Selectivity (*S*) of the reesterification of compound *III*f at 20°C in aqueous methanol (*x* mole fraction of methanol)

<i>x</i> (CH ₃ OH)	0.059	0.123	0.183	0.281	0.360	0.457	0.567	0.692	0.835
<i>S</i>	0.185	0.350	0.415	0.552	0.633	0.675	0.760	0.793	0.900

phosphorus, the rate constant for *o*-tolyl esters is about 1.5 to 2.5 times lower than that for phenyl esters²⁷. The solvolysis rate constants for phenyl and *o*-tolyl esters in 50% (wt) ethanol are compared in Table VII. As seen, the *o*-tolyl esters react much more slowly than the phenyl esters. These results confirm²⁷ the presence of pentavalent phosphorus in the solvolysis intermediate.

Reesterification. According to Ingold²⁸, in a binary solvent, a highly reactive intermediate reacts non-selectively with both the nucleophilic components. The method gives good results for the system water-methanol¹¹. The reesterification reaction of *IIf* in 50% (wt) ethanol (mole fraction of alcohol $x = 0.281$) takes place to the extent of 10%. If we define the selectivity of the reesterification reaction S as the ratio of moles of the ester to the sum of moles of all products ($S = n(\text{ester})/\sum n$) then in 50% ethanol ($x = 0.281$) the selectivity $S = 0.100$. In the given water-methanol mixtures, the reesterification proceeds with selectivities given in Table VIII. On going from methanol to ethanol, the selectivity of reesterification reaction decreases more than five times. This finding excludes the highly reactive imido derivative with trivalent phosphorus as the possible reaction intermediate and thus again confirms the S_N2 mechanism of the studied solvolysis. The above-mentioned results can be summarized in Scheme 1.



R = CH₃, C₂H₅

SCHEME 1

Similar schemes can be written for other aryl esters of substituted diamidophosphoric acids. Using the known dissociation constants, we can convert the rate constants given in Tables III–V into the constants k' which are the sum of constants for the hydrolytic and reesterification reactions, $k' = k_{\text{hydr.}} + k_{\text{reest.}}$. The experiments were carried out so as the subsequent hydrolysis of alkyl esters to acids was not observed (using suitable wavelengths) or the reaction was interrupted in time so as the yields of the alkyl esters were not decreased. The different reactivity of triaryl phosphates, diaryl amidophosphates and aryl diamidophosphates is due to replacement of the RO-group by the RNH-group. This is in accord with the charge transfer from nitrogen to phosphorus which fills the electron deficit at the electrophilic center of the molecule and thus also reduces the reactivity.

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