Substitution Effect on Solvolysis Rate of Arylamides of Phosphoric Acid

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Dedicated to Professor RNDr. K. Dostál, DrSc., in honour of his 70th birthday

The rate of alkaline solvolysis of some diaryl esters of arylamides of phosphoric acid was measured in the mixtures water—methanol and water—2-propanol. The second-order rate constant k_{OH}° of hydrolytic and k_{MeO}° of methanolic reactions were calculated from measured rate constants k_{exp}, known concentration ratio of reaction products, and known ratio of lyate ions activities. The effect of methyl group in position 2 or 4 on the change of rate constants is discussed.

According to literature [1], the effect of methyl group in position 2 on slowing down the hydrolytic reaction of aryl esters of phosphoric acid consists in steric reasons. The presence of 2-propyl and 2-butyl groups leads to a decrease of reaction rate of S_N2 reactions as well [2]. We tried to prove these conclusions with diaryl esters of arylamides of phosphoric acid by parallel reactions in the mixtures water—methanol and water—2-propanol [3]. The method of parallel reactions seems to be suitable for identification of steric effects but in this particular case the results have to be ascribed to another than steric effect of CH_3 group in position 2. Experimentally, the paper [1] is based on the rate constants measurements. Therefore it seems to be promising to consider once again the possibility of apparent steric hindering of nucleophilic centre by CH_3 groups in position 2 according to the rate constants measurement. Additional data to those given in [1] would be obtained, which can be used for estimating the steric effects.

EXPERIMENTAL

Diaryl esters of arylamides of phosphoric acid with the general structure $(R^1O)_2P(O)NHR^2$, where $R^1 = R^2 = C_6H_5$ (*I*); $R^1 = C_6H_4—CH_3$-*o*, $R^2 = C_6H_5$ (*II*); $R^1 = C_6H_4—CH_3$-*p*, $R^2 = C_6H_5$ (*III*); $R^1 = C_6H_5$, $R^2 = C_6H_4—CH_3$-*o* (*IV*); $R^1 = R^2 = C_6H_4—CH_3$-*o* (*V*); $R^1 = C_6H_5$, $R^2 = C_6H_4—CH_3$-*p* (*VI*); $R^1 = R^2 = C_6H_4—CH_3$-*p* (*VII*), were the same compounds as used in [3]. The purity was determined by measurement of melting point and by elemental analysis. The obtained data were in accordance with theory.

For the kinetic measurements the solutions of compound of concentration 2.5 x 10^{-4} mol dm^{-3}

were prepared in diluted methanol (*w* = 60, 70, 80, 90 %) and 2-propanol (*w* = 70 %). Further, 0.2 ± 0.0003 M solutions of NaOH (Lachema, Brno, anal. grade) were prepared in the same solvents. The concentration of the hydroxide was determined by titration. Distilled water, methanol, and 2-propanol (all from Lachema, Brno, anal. grade) were used for solutions preparation. The reaction mixtures were made by mixing of the same volumes of diaryl ester solutions with hydroxide solutions. Both solutions were tempered to 25 °C before measurement. The analysis of the mixture was done using a spectrophotometer SP 8-100 (Pye—Unicam). The experiment was performed at 25 °C at the wavelength equal to that of maximal absorbance of formed phenolate or cresolate ion. The rate constants were calculated from the equation

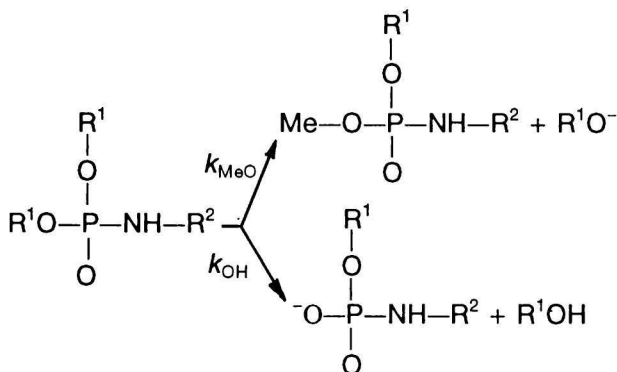$$A = B_1 \exp(1 - B_2 t) + A_\infty \qquad (1)$$

A being the absorbance in the time *t*, B_1 a constant, B_2 the rate constant (k_{exp}) and A_∞ the absorbance in *t* = ∞. The values of B_1, B_2, A_∞ have been calculated according to the nonlinear least squares method. The results obtained are statistically significant with the probability level of 99.9 %.

RESULTS AND DISCUSSION

The values of k_{exp} calculated according to eqn (*1*) and used wavelengths are shown in Table 1. According to [3], hydrolysis and alcoholysis proceed simultaneously in the mixture of water—methanol as seen in Scheme 1. Hydrolysis only proceeds in the system water—2-propanol because of steric reasons. Therefore in the water—methanol system

Table 1. Used Wavelengths and Rate Constans of Solvolysis of Diaryl Esters of Arylamides of Phosphoric Acid k_{exp} Measured at (25 ± 0.1) °C in the Given Medium

Compound	λ/nm	$k_{exp} \cdot 10^5/s^{-1}$				
		w(Methanol)/%				w(2-Propanol)/%
		60	70	80	90	70
I	288	18.6	18.1	17.7	16.4	6.07
II	294	3.22	2.52	2.43	1.93	1.00
III	296	6.82	7.13	6.14	4.49	2.90
IV	288	53.0	49.9	47.8	43.5	31.0
V	294	4.93	3.69	3.22	2.26	1.60
VI	288	10.1	10.0	9.95	8.82	4.60
VII	296	7.33	7.40	7.02	5.86	5.39

Table 2. Rate Constants k_{OH}° and k_{MeO}° (dm^3 mol^{-1} s^{-1}) Calculated According to the Data from Table 1

Compound	w(Methanol)/%			
	60		70	
	$k_{OH}^\circ \cdot 10^4$	$k_{MeO}^\circ \cdot 10^4$	$k_{OH}^\circ \cdot 10^4$	$k_{MeO}^\circ \cdot 10^4$
I	6.66	25.1	7.18	21.8
II	2.30	3.72	3.05	2.35
III	3.91	8.38	3.96	8.19
IV	7.80	77.3	6.76	64.4
V	4.54	5.14	2.27	4.16
VI	3.97	13.4	4.88	11.7
VII	4.37	8.92	4.12	8.49

Compound	w(Methanol)/%				w(2-Propanol)/%
	80		90		70
	$k_{OH}^\circ \cdot 10^4$	$k_{MeO}^\circ \cdot 10^4$	$k_{OH}^\circ \cdot 10^4$	$k_{MeO}^\circ \cdot 10^4$	$k_{OH}^\circ \cdot 10^4$
I	9.40	19.2	9.59	16.9	40.5
II	4.50	2.06	5.51	1.66	6.67
III	4.82	6.38	5.47	4.41	19.3
IV	4.08	55.5	6.60	46.3	207
V	4.37	3.01	4.54	2.09	107
VI	7.80	10.3	10.6	8.69	30.7
VII	5.71	7.25	4.73	5.95	35.9

Scheme 1

$$k_{exp} = k_{OH} + k_{MeO} \qquad (2)$$

k_{OH} and k_{MeO} being the rate constants of hydrolysis and alcoholysis, respectively. In the system water—2-propanol

$$k_{exp} = k_{OH} \qquad (3)$$

Since the portions of reaction products of methanolic and hydrolytic reactions are known, the following equation is valid

$$c(ester)/c(salt) = k_{MeO}/k_{OH} \qquad (4)$$

assuming the first order of both reactions to the substrate. This assumption was proved for diaryl esters of arylamides of phosphoric acid in several papers [4, 5]. A system of two equations with two roots is formed by eqns (2) and (4). The calculation of k_{MeO} and k_{OH} is easy.

Both reactions proceed under a substantial excess of nucleophile. Therefore

$$k_{MeO} = k_{MeO}^\circ\, c(MeO^-), \quad k_{OH} = k_{OH}^\circ\, c(OH^-) \qquad (5)$$

The constants k_{MeO}° and k_{OH}° could be calculated from eqn (5) if the concentration ratio of lyate ions as well as overall base concentration were known. However, the concentration ratio of lyate ions is

unknown. Therefore the ratio of their activities was used, which is known with sufficient reliability [6]. If Q is the activity ratio of lyate ions, the equation

$$c(MeO^-)/c(OH^-) = Q \qquad (6)$$

is valid. At the same time the overall base concentration is equal to

$$c(NaOH) = c(MeO^-) + c(OH^-) \qquad (7)$$

Again, a system of two equations with two roots $c(MeO^-)$ and $c(OH^-)$ has been formed, the calculation being simple. Inserting the results into eqn (5), k_{MeO}° and k_{OH}° are calculated. The results of calculation are given in Table 2. The dependence of log k_{OH}° and log k_{MeO}° on the reciprocal value of relative permittivity of medium is shown in Figs. 1 and 2. It is evident from Table 2 that the values k_{OH}° of the group of compounds in question are decreasing with rising content of water in the mixed solvent. The exceptions are the compounds IV and V which are (2-methylphenyl)amides of phosphoric acid. This is the reason why the dependence of log k_{OH}° vs. $1/\varepsilon_r$ is given in Fig. 1 for these two compounds. Among other derivatives, only the compounds I and VII were chosen to show the linear dependence of log k_{OH}° vs. $1/\varepsilon_r$. This dependence is linear also for other compounds not shown in the figure. Hence it is apparent that the hydrolytic constants in the mixture water—2-propanol (at $1/\varepsilon_r = 0.035$) deviate from the linear dependence of logarithms of hydrolytic constants vs. $1/\varepsilon_r$ in the system water—methanol.
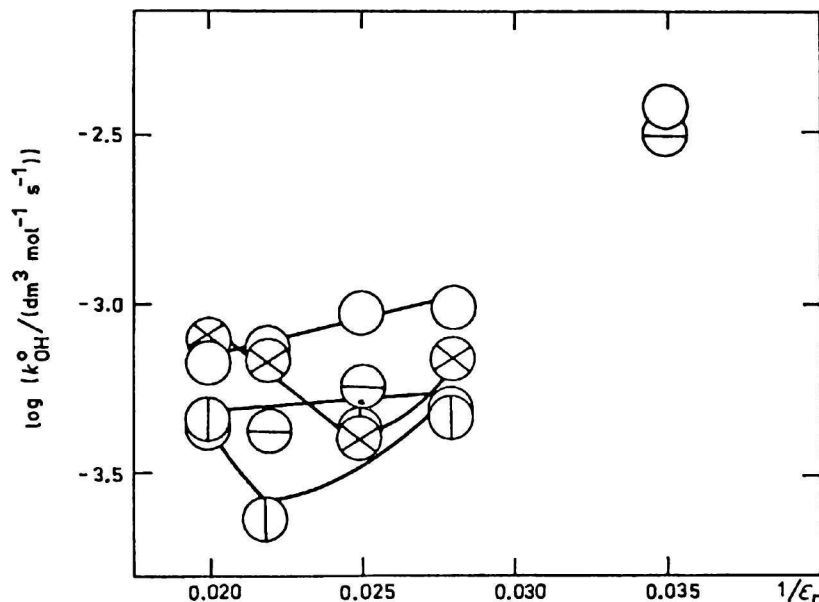
Fig. 1. The dependence of log k_{OH}° on $1/\varepsilon_r$ of the medium for compounds *I* ($\bigcirc$), *IV* ($\otimes$), *V* ($\oplus$), *VII* ($\ominus$).

This result is different from the observation of another very similar group of compounds where it was found that the hydrolytic constants were situated on the same line if measured in water—ethanol or water—2-propanol mixture [7]. The results from paper [7] were used for calculation of k_{OH}° values in the mixture water—2-propanol shown in Table 2.

The effect of CH_3 group on the rate of solvolytic reactions is very interesting. If aryls of ester groups are substituted by methyl group, the rate of solvolytic reaction is lower (Table 2) or virtually unchanged. The more pronounced changes are observed in k_{MeO}° values. It is assumed that the

Fig. 2. The dependence of log k_{MeO}° on $1/\varepsilon_r$ of the medium for compounds *I—VII* ($\bigcirc$, $\oslash$, $\bullet$, $\otimes$, $\oplus$, $\oplus$, $\ominus$), respectively.

reason for rate constant decrease is the induction effect of methyl group. The substitution at the aromatic ring of phenylamido group in position 4 by methyl group leads again to the decrease of rate constants of solvolytic reactions, but the substitution of phenylamido group in position 2 results in complicated effects. These are obvious from comparison of the rate constants of compounds *I* and *IV* in Table 2. This substitution affects the nonlinear dependence of log k_{OH}° on $1/\varepsilon_r$ of compound *IV* (Fig. 1) which is difficult to discuss. Generally, the k_{OH}° value of compound *IV* is not too different from the value of model compound *I* in the region of investigation. The constant k_{MeO}° is influenced to much higher degree by the substitution since the value is much higher for compound *IV* than for *I*. Similar although less pronounced effects have been observed when comparing the rate constants of compounds *II* and *V*. It was shown [8] that solvolysis of diesters of arylamides of phosphoric acid proceeds by S_N2 mechanism, unstable intermediate being a trigonal bipyramid with entering and leaving moiety positioned in tops. If so, the steric effects of *II* and *IV* should retard the solvolysis to the same extent, when compared to model compound *I*. However, the experimental results do not confirm this assumption, since faster methanolysis was observed with *IV*. This is in contradiction with the published data [1] on steric hindering of the nucleophilic centre by CH_3 group in position 2. Therefore, the steric hindering of the phosphorus atom by CH_3 group in position 2 cannot be considered as proved in solvolyses proceeding by S_N2 mechanism. More experiments will be
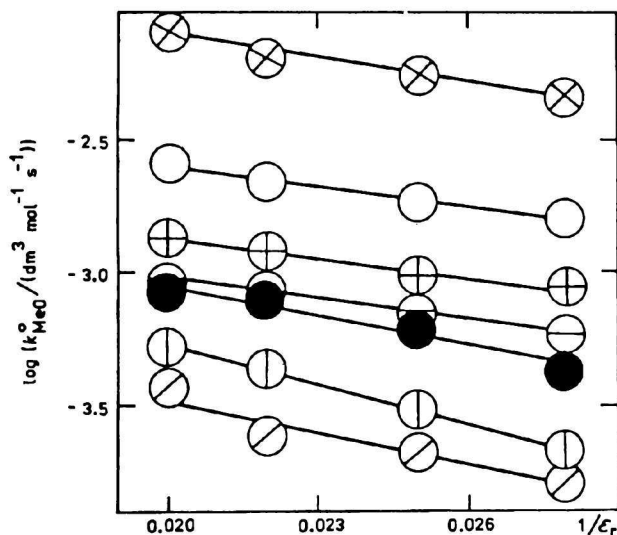
necessary to enable a discussion of the effect on the reaction rate in detail.

The given conclusions agree with the results of our previous paper [3]. Moreover, since the value of $k°$ is used for discussion of effects, more detailed view of the investigated problem is possible.

An additional conclusion can be drawn from the given experimental values. The equation

$$c(\text{ester})/c(\text{salt}) = (k^°_{\text{MeO}}/k^°_{\text{OH}})\,(c(\text{MeO}^-)/c(\text{OH}^-))\quad(8)$$

is derived using eqns (4) and (5). The ratio of concentrations of lyate ions can be calculated using eqn (8) according to the concentration ratio of reaction products, if $k^°_{\text{MeO}}$ and $k^°_{\text{OH}}$ are known (usually in one-component solvent) assuming that the ratio of both constants does not change if the solvent is changed. The method based on eqn (8) and the above-mentioned assumption has led to the first information [9—11] on the ratio of lyate ions concentrations. Obviously (Figs. 1 and 2), the dependence of rate constants on solvent is intransparent. The method can be considered as only semiquantitative and can be recommended only if all other procedures fail.

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