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SOLVENT EFFECT ON THE RATE OF ESTER INTERCHANGE OF

p-NITROPHENYLDIETHYLPHOSPHATE

V. E. Bel'skii, F. G. Valeeva, L. A. Kudryavtseva, and B. E. Ivanov UDC 541.12.038.2:541.127: 542.951.3:547.26'118

The reaction of p-nitrophenyldiethylphosphate with sodium phenolate takes place readily in aprotic polar solvents. Bimolecular rate constants of this reaction increase with increased concentration of the phenolate in such solvents as dimethylsulfoxide (DMSO), dimethylformamide (DMF), or hexamethylphosphoric amide (HMPA), but decrease in acetonitrile or acetone; this is caused by the association of sodium phenolate, and the different reactivities of free ions and ion pairs. The addition of 18-crown-6 to the reaction mixture decreases the reaction rate, because of the reduced reactivity of the complex formed by the crown ether with the phenolate ion pair.

Various authors have investigated the kinetics and mechanism of ester interchange of acids of tetracoordinated phosphorus [1-9]. A feature of such reactions with nucleophiles of the phenolate (PhO⁻) type is the similarity of the chemical properties of the displaced groups to those of the anions entering into nucleophilic attack on the P atom. The complexity of the ester interchange mechanism is evinced by the fact that in a DMF medium, cis- and trans-2-p-nitrophenyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphoranes react with Na p-nitrophenolate and K p-cresolate to form products with inversion and retention of conformation [1]. The inverted product is obtained by a reaction proceeding through a trigonal bipyramidal intermediate, or else through a transition state of that same structure. The presence of a certain amount of product with retained conformation in [1, 2] was explained by a parallel reaction course including such possible variants of the mechanism as pseudorotation of ligands in the intermediate, splitting off of the leaving group from an equatorial position of the bipyramid, or the parallel formation of an intermediate with a square-pyramidal structure.

Phenolates readily react with esters of diphenylphosphinic acid [3, 4] and substituted phosphonic acids [5, 6] in aqueous solutions, but reactions of the esters with hydroxide ions and amines, present as buffering components, also occur. The rate constants of the phenyl ester interchange reactions depend on the nature of the phenolate ions participating in nucleophilic attack on the P atom, and of those splitting off as a result of the reaction; the rate constants show a Brönsted dependence on the basicity (pK_a values) of the nucleophiles and of the exiting groups [4, 6]. Esters of phosphoric acid usually react more slowly than esters containing alkyl groups on the P atom [7, 8].

Comparing the rate constants of the reaction of p-nitrophenyldiphenylphosphate with PhONa in water [8] and acetonitrile (AN) [9], it can be stated that changing the reaction medium from water to an aprotic polar solvent increases the reaction rate more than 1800 times. In this connection, it seemed interesting to do a broader study of solvent effects on the rate of ester interchange of esters of phosphorus acids. With this aim, we have

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TABLE 1. Rate Constants of the Reaction of PhONa with p-Nitrophenyldiethylphosphate at 25°C in Polar Aprotic Solvents, and the Effect of Additions of 18-Crown-6 Ether

		and the second					
[PhONa] [18-Crown-6]		_1	<pre>k₂, liter/(mole·sec)</pre>				
mole/liter		^k ·10 ⁻ , sec ⁻¹					
	Aceton	itrile					
$\begin{array}{c} 0,00455\\ 0,00705\\ 0,0140\\ 0,0179\\ 0,0179\\ 0,0228\\ 0,0281\\ 0,0352\\ 0,0470\\ 0,0911\\ 0,139\\ 0,198\\ 0,264 \end{array}$	0,211	0,520 0,943 1,53 1,64 0,714 1,98 2,32 2,45 2,86 4,06 5,22 7,60 8,90	$\begin{array}{c} 1.14\\ 1.34\\ 1.09\\ 0.916\\ 0.400\\ 0.868\\ 0.826\\ 0.696\\ 0.609\\ 0.446\\ 0.376\\ 0.383\\ 0.337\\ \end{array}$				
Acetone							
$\begin{array}{c} 0.0034\\ 0.0068\\ 0.0106\\ 0.0106\\ 0.0204\\ 0.0212\\ 0.0212\\ 0.0212\\ 0.0340\\ \end{array}$	0,211	$\begin{array}{c} 1,53\\ 3,14\\ 3,29\\ 0,307\\ 5,69\\ 6,20\\ 0,374\\ 6,57\end{array}$	4,50 4,63 3,10 0,290 2,79 2,92 0,176 1,93				
	Dimethyls	ulfoxide					
$\begin{array}{c} 0,0074\\ 0,0119\\ 0,0449\\ 0,0238\\ 0,0276\\ 0,0276\\ 0,0276\\ 0.0297\\ 0.0397\end{array}$	- - - 0,451 -	$\begin{array}{c} 0,257\\ 0,536\\ 0,915\\ 1,79\\ 2,04\\ 1,07\\ 2,73\\ 4,10\\ \end{array}$	$\begin{array}{c} 0.347\\ 0.450\\ 0.616\\ 0.752\\ 0.730\\ 0.390\\ 0.919\\ 1.03\end{array}$				
Dimethylformamide							
$\begin{array}{c} 0.0100\\ 0.0140\\ 0.0140\\ 0.0230\\ 0.0295\\ 0.0295\\ \end{array}$	0,113 	1,78 4,18 0,747 7,37 12,1 2,49	1,78 2,99 0,534 3,20 4,10 0,845				
H	examethylphosp	horic triamide					
0.00250 0.00500 0.00630 0.00760 0.0100 0.0100 0.0150 0.0171	0,101 - 0,178 0,202 0.358 0,367	$\begin{array}{c} 0.090\\ 0.433\\ 0.075\\ 2.50\\ 5.50\\ 0.402\\ 11.6\\ 3.30\\ 19.1\\ 5.40\\ 7.10\\ \end{array}$	$\begin{matrix} 0.360\\ 0.860\\ 0.150\\ 3.97\\ 7.24\\ 0.533\\ 11.6\\ 3.30\\ 12.7\\ 3.60\\ 4.15\end{matrix}$				

studied the kinetics of the reaction of p-nitrophenyldiethylphosphate with PhONa in some solvents that are often used for nucleophilic substitution reactions.

EXPERIMENTAL

Previously dried and distilled solvents were used for the experiments. PhONa was prepared by reacting phenol with metallic Na in petroleum ether and subsequently distilling off the solvent. The experiments were performed with freshly prepared solutions of PhONa, since the latter is unstable in the solvents used. The kinetics were followed spectrophotometrically, by measuring the optical density D of the solutions at 23,000 cm⁻¹ (absorption of the p-nitrophenolate formed in the reaction) on a "Specord UV-VIS" instrument. The

TABLE 2. Bimolecular Rate Constants k_2 , Calculated over Definite Intervals of PhONa Concentration, According to Eq. (2)

Solvent	[PhONa]. mole/liter	k ₂ * liter/(mole· sec)	۵	N **	r **
Acetonitrile Acetone Dimethylsulfoxide Dimethylformamide Hexamethylphosphoric triamide	0.014-0.264 0.0068-0.034 0.0119-0.0397 0.0100-0.0295 0.0050-0.0150	$\begin{array}{c} 0.267 \pm 0.09 \\ 1.42 \pm 0.35 \\ 1.25 \pm 0.10 \\ 5.01 \pm 0.53 \\ 19.1 \pm 1.2 \end{array}$	$\begin{array}{c} 0,0131\pm 0,0010\\ 0,0233\pm 0,0072\\ -0,0105\pm 0,0026\\ -0,032\pm 0,011\\ -0,090\pm 0,012 \end{array}$	10 5 6 4 5	0,997 0.922 0,987 0.989 0,994

*25°C.

**N is the number of values of k used in the calculations, r is the correlation coefficient.

solutions were thermostated (±0.5°C) in quartz cuvettes with a ground glass stopper. The experiments were performed with initial concentrations of ester $C_0 \sim 10^{-4}$ mole/liter, PhONa > $20C_0$. The change of D with time (t) during the course of the reactions corresponded to a first-order kinetic equation:

$$\ln \left(D_{\infty} - D \right) = -kt + \ln \left(D_{\infty} - D_{0} \right), \tag{1}$$

where D is the optical density at the moment t from the start of the measurements, D_0 and D_{∞} are the values of D at t = 0 and t > 7 k⁻¹, and k is the pseudo-first-order rate constant. The calculation of k in the kinetic equation was performed by a weighted least-squares method [10], using an original program written for an "Élektronika DZ-28" micro-computer.

RESULTS AND DISCUSSION

In aqueous solutions, ester interchange reactions of acids of tetracoordinated phosphorus are characteristically of the first order in phenolate ion [3-6], as follows from the constancy of the bimolecular rate constant $k_2 = k/C$ on changing the phenolate ion concentration (C). In all the aprotic solvents used, the values of k_2 are not constant, but change severalfold over the working range of concentrations of PhONa (Table 1). In such solvents as AN and acetone (A), the values of k_2 diminish with increased concentration of PhONa in the solution, but in DMSO, DMF, and HMPA media they increase markedly.

The variation of k_2 is caused by association of PhONa in the solvents, where it forms ion pairs and more complicated conglomerates [1, 9]; these associated forms dissociate at low concentrations into free ions. Ions and ion pairs can differ very much in reactivity [11]. The decrease in k_2 in AN and A shows that the reactivity of phenolate decreases on association. In contrast to this, the associates are more active than the free ions in DMSO, DMF, and HMPA; therefore the values of k_2 increase with the concentration of phenolate.

It should be mentioned that in all the solvents investigated the dependence of k on phenolate concentration is linear and corresponds to the equation

$$k = k_2 \cdot C + a, \tag{2}$$

where a is a constant whose value is determined by the ratio of reactivities of free and associated ions.

Equation (2) is adequately obeyed at sufficiently high degrees of association, and makes it possible to estimate values of k_2 for PhONa in the associated state (Table 2). The values of k_2 , calculated according to Eq. (2) by the method of least squares, vary markedly according to the solvent used; for example, in HMPA the value of k_2 is 60 times higher than in AN.

Determination of the rate constants in the presence of added amounts of 18-crown-6 (which interacts with Na⁺) is of interest in order to estimate the reactivity of PhO⁻ when its cation is solvated by crown ether. Sub and Mun [9] observed retardation of the

reaction of PhONa and PhOK with p-nitrophenyldiphenylphosphate in AN in the presence of crown ethers. However, examples are also known of acceleration of phenolate reactions by addition of crown ethers [12].

The rate constants of the reaction studied by us diminish in the presence of 18-crown-6 in all the solvents tested (Table 1). The values of $k_2 = k/C$ vary with the PhO⁻ concentration in the same way as in the absence of crown ether. The diminution in the values of k_2 in the presence of crown ether in AN and A media, where the free ions are more reactive than the associated ions, indicates that crown ether, even when present in excess over PhO⁻, does not shift the equilibrium over to the side of free ions. Apparently, the effect of crown ether on the reaction is a result of its formation of a complex with the phenolate ion pair. The reactivity of such complexes in the system studied is less than that of the ion pairs. We should note that the existence of similar complexes of crown ethers with ion pairs has been established in some cases [12].

Thus, the investigation performed indicates that ester interchange reactions of esters of acids of tetracoordinated phosphorus proceed several thousand times faster in aprotic polar solvents than in aqueous solutions. HMPA gives the fastest reaction rate.

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