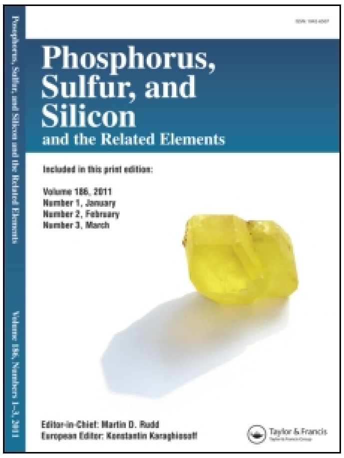

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XXXIV. SOLVENT EFFECT ON ALKALINE HYDROLYSIS OF 2-PROPYL- AND 2-ISOPROPYL-2-OXO-1,3,2-DIOXAPHOSPHORINANE

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To cite this Article Liao, Xiugao , Li, Shusen and Yuan, Chengye(1989) 'STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XXXIV. SOLVENT EFFECT ON ALKALINE HYDROLYSIS OF 2-PROPYL- AND 2-ISOPROPYL-2-OXO-1,3,2-DIOXAPHOSPHORINANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 42: 1, 53 — 61

To link to this Article: DOI: 10.1080/10426508908054876

URL: http://dx.doi.org/10.1080/10426508908054876

Phosphorus, Sulfur, and Silicon, 1989, Vol. 42, pp. 53–61
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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XXXIV. SOLVENT EFFECT ON ALKALINE HYDROLYSIS OF 2-PROPYL- AND 2-ISOPROPYL-2-OXO-1,3,2-DIOXAPHOSPHORINANE

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(Received April 14, 1988; in final form July 12, 1988)

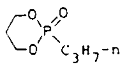
Alkaline hydrolyses of 2-propyl-2-oxo-1,3,2-dioxaphosphorinane and 2-iso-propyl-2-oxo-1,3,2-dioxaphosphorinane were studied in aqueous mixtures of dioxane, dimethylsulfoxide and acetone. The rate constants were determined at various temperatures, and thermodynamic reaction parameters were evaluated. The rate constant (k) of hydrolysis is found to be a function of both the polarity of the solvent mixture and the ratio volume of aprotic solvent and water in the mixture represented by ϕ value. The rate of hydrolysis can be expressed as a function of the dielectric constant as well as due to the hydration by the organic solvent molecules, making the HO^- stronger nucleophilic. The hydrolysis demonstrates an isokinetic relationship, suggesting that the reaction mechanism is similar in the various solvent systems studied.

Key words: 2-Alkyl-2-oxo-1,3,2-dioxa phosphorinane; alkaline hydrolysis; kinetic study; solvent effects; reaction-mechanism.

INTRODUCTION

The hydrolysis of carboxylic esters in various solvent systems was extensively studied by Costenau,[1–4] esters of various phosphorus acids are, however, less investigated. The solvent effect on the alkaline hydrolysis of aryl diphenylphosphinate and aryl dimethylphosphinothioates are reported by Istomin.[5–7] Aksnes *et al.* have investigated the solvent effect on the hydrolysis of phosphonium salt in a series of aqueous mixture.[8–10] We described the substituent effect in the alkaline hydrolysis of 2-alkyl-2-oxo-1,3,2-dioxaphosphorinane and -phosphetane in 50% aqueous dioxane and 50% aqueous dimethyl sulfoxide (DMSO) respectively.[11,12] However, there are no available data concerning the solvent effect in the hydrolysis of cyclic esters of phosphonic acids.

In this paper, we report a study of the hydrolysis of 2-propyl-2-oxo-1,3,2-dioxaphosphorinane **1** and 2-isopropyl-2-oxo-1,3,2-dioxa-phosphorinane **2** in different solvents systems at various temperatures.



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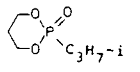

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RESULTS AND DISCUSSIONS

Alkaline hydrolyses of 2-propyl- and 2-isopropyl-2-oxo-1,3,2-dioxaphosphorinane (**1**, **2**) were carried out in various aqueous aprotic solvents, with various volume ratio, ϕ, of aprotic solvent and water. The second order rate constants of alkaline hydrolysis of **1** and **2** were determined by potentiometric titration (Table I).

The experimental data in Table I show that the rate constants (k) decrease with increasing ϕ values as long as $\phi < 0.5$, whereafter the rate constants again start to increase. Logarithmic plots of the rate constants against ϕ in Figures 1–3, show that the rate constants (k) of the cyclic phosphonate **1** are more strongly influenced by the ϕ values in comparison with carboxylic esters.

During hydrolysis, the chemical environment around phosphorus in cyclic phosphorus ester is quite different from that around the carbonyl carbon in carboxylic esters. The mechanism of hydrolysis of cyclic as well as acyclic phosphate or phosphonate[13–18] involves transformation from a tetrahedral to a dipyramidal placement of the substituents linked to phosphorus, while the hydrolysis of carboxylic esters consists of the conversion of trigonal to tetrahedral configuration of the carbon atoms. When $\phi < 0.5$, the rate of **1** can be expressed as a function of the dielectric constant of the solvent mixture. According to the theory for the ion dipole interaction, $\log k$ is found to depend on the dielectric constant.[19]

$$\log k_D = \log k_0 + Ze\,\mu/DkTr^2 \qquad (1)$$

Where $\log k_D$ is the rate constant in the solvent mixture with dielectric constant D, $\log k_0$ is the rate constant in the mixture with $D = \infty$, Ze represents the charge of the ion, and μ represents the dipole of the polar molecule. In the alkaline

TABLE I

Rate constants for alkaline hydrolysis of 2-propyl-2-oxo-1,3,2-dioxaphosphorinane in various solvent systems with different ϕ value

	k in various ϕ of Acetone-H_2O						
Temp (K)	0	0.20	0.30	0.50	0.60	0.70	0.80
302.7	58.1	51.6	47.5	45.2	52.7	70.1	122.1
298.7	46.6	40.2	40.5	36.8	41.3	56.3	74.2
292.7	28.6	26.5	23.6	24.2	23.6	32.5	42.7

	k in various ϕ of DMSO-H_2O					
Temp (K)	0	0.10	0.25	0.40	0.50	0.65
302.7	58.1	58.3	55.1	54.6	55.1	134.6
298.7	46.6	47.3	44.0	43.7	43.9	63.8
292.7	28.6	28.6	26.7	25.4	25.1	35.1

	k in various ϕ of Acetone-H_2O						
Temp (K)	0	0.20	0.35	0.40	0.50	0.65	0.80
302.7	58.1	44.1	34.5	32.9	35.2	39.2	59.2
298.7	46.6	39.6	33.3	29.4	27.7	31.7	48.9
292.7	28.6	22.3	17.3	17.2	15.7	18.0	27.5

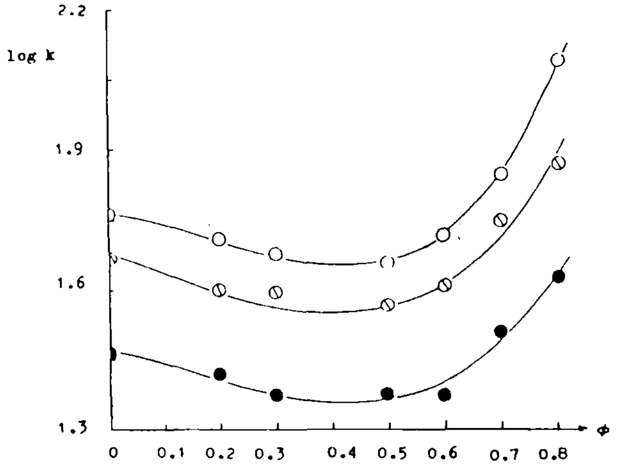

FIGURE 1 Plot of log k of 1 as function of ϕ of Dioxane-H_2O ○—T = 302.7, ⊘—T = 298.7, ●—T = 292.7

hydrolysis of **1**, *Ze* of the nucleophile, HO^-, in Equation (1) is -1, and $\log k_D$ will decrease linearly with increase of the D of the solvent. When $\phi < 0.5$, the hydration of the increasing amount of dipolar solvent molecules becomes more important than the decrease of the dielectric constant of the solvent mixture. Under such conditions, large number of water molecules will be strongly bonded and immobilized by dipolar organic solvent molecules. The hydration of the HO^- anion is therefore weakened, and the nucleophilicity of the less hydrated hydroxyl anion is enhanced, giving rise to an increase of the hydrolysis. The rate curve as function of ϕ will accordingly pass through a minimum around $\phi \sim 0.5$. The dielectric constants of the solvent mixture was evaluated from the data of

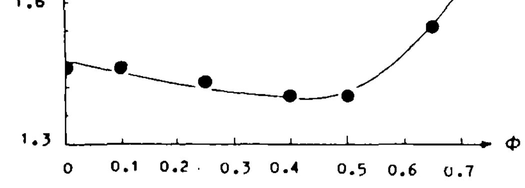

FIGURE 2 Plot of log k of 1 as function of ϕ of DMSO—H_2O ○—T = 302.7, ⊘—T = 298.7, ●—T = 292.7

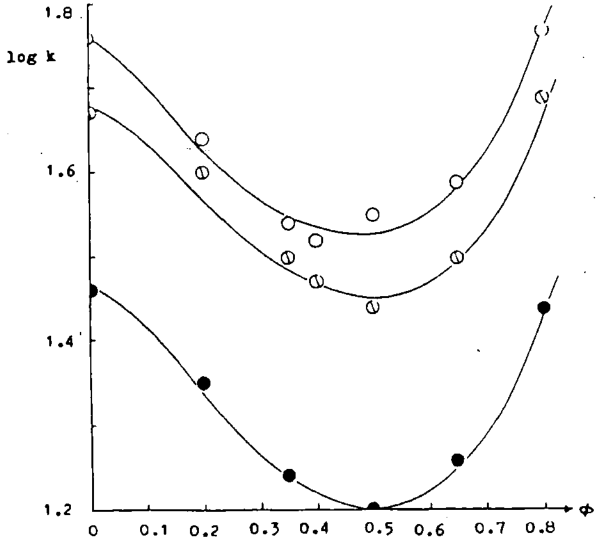

FIGURE 3 Plot of log k of 1 as function of ϕ of Acetone-H_2O ○—T = 302.7, ⊘—T = 298.7, ●—T = 292.7

Akerlof[20–22] (see Table II), and plotting $\log k$ versus $100/D$ of the different solvent mixtures gave rate curve which are qualitatively in agreement with Akerlof's result (Figures 4, 5). Istomin[5–7] showed that for p-substituted phenyl dimethylphosphinothioates the correlation between $\log k$ and D was dependent on the nature of the substituents on the phenyl group. Since the p-substituted phenoxy radical served a leaving group, a better leaving group will contribute to increase of the rate constant at $\phi > 0.5$ of the mixed solvent markedly.

In order to examine the influence of the steric effect of the alkyl group on the k value in dioxaphosphorinanes the hydrolysis of **2** was carried out in DMSO and dioxane in the region of $\phi = 0.00$–0.80. As shown in Table III, and Figures 6 and 7, the effect of the solvent mixture on the hydrolysis of **2** was similar to that of **1** indicating that the mechanism of the alkaline hydrolysis of **1** and **2** is identical.

TABLE II

Dielectric constant of solvent mixture

	D in various ϕ of dioxane-H_2O								
Temp (K)	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80
293.2	69.16	65.68	62.38	59.24	56.26	53.43	50.75	48.20	45.77
303.2	59.34	56.24	53.30	50.52	47.88	45.38	43.01	40.76	38.63

	D in various ϕ of Acetone-H_2O						
Temp (K)	0.00	0.20	0.35	0.40	0.50	0.65	0.80
323.2	76.73	67.45	59.47	55.73	50.73	40.75	31.10
298.2	78.54	69.09	61.04	57.18	52.05	41.80	32.05
293.2	80.37	70.77	62.48	58.59	53.41	42.93	32.80

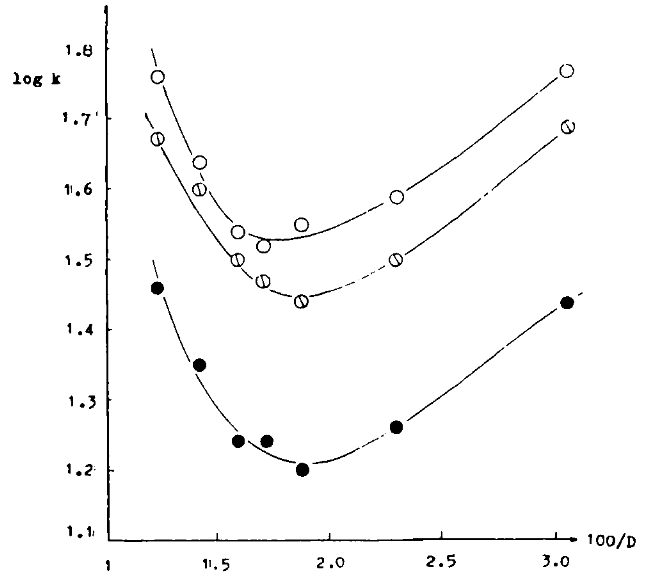

FIGURE 4 Plot of log *k* of 1 versus 100/D value of Acetone—H_2O ○—T = 302.7, ⊘—T = 298.7, ●—T = 292.7

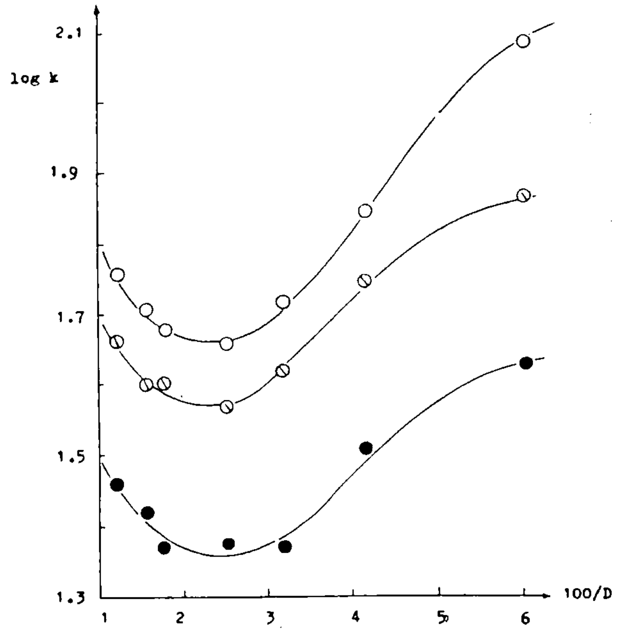

FIGURE 5 Plot of log *k* of 1 versus 100/D value of Dioxane—H_2O ○—T = 302.7, ⊘—T = 298.7, ●—T = 292.7

TABLE III

Rate constants for alkaline hydrolysis of 2-isopropyl-2-oxo-1,3,2-dioxaphosphorinane **2** over various mixture solvents at 323.7(K)

	k in various ϕ							
Solvent	0.00	0.20	0.30	0.35	0.40	0.50	0.65	0.80
Dioxane-H_2O	8.54	7.58	—	7.38	—	9.66	12.6	18.1
DMSO-H_2O	8.54	8.51	8.70		9.52	12.2	22.5	111.5

However, the minimum in the rate constant of **2** was shifted to $\phi \approx 0.3$, and the gradient of the rate decrease was smaller than for **1**. However, the gradient of the rate increase of **2** is smaller than for **1**. This indicates the hydration of the solvent molecules is more important than the dielectric constant effect of the solvent on the hydrolytic process of **2**. It can be rationalized by the fact that the influence of dielectric constants was of less importance for iso-propyl group than for *n*-propyl group. Therefore, in order to increase the rate of hydrolysis for the phosphorus

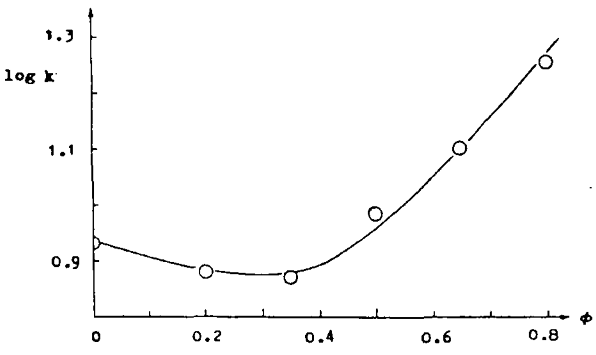

FIGURE 6 Plot of log k of **2** as function of ϕ of Dioxane-H_2O

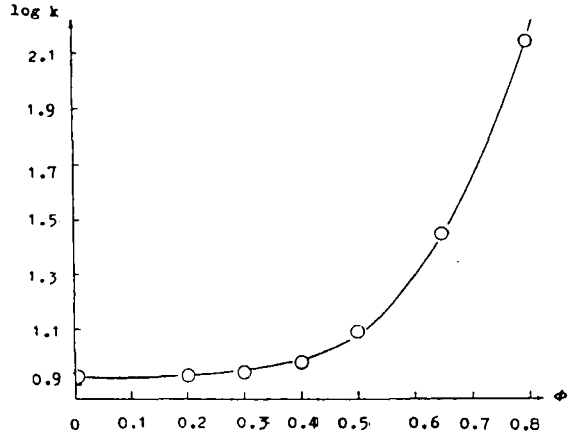

FIGURE 7 Plot of log k of **2** as function of ϕ of DMSO-H_2O

TABLE IV

Thermodynamic functions of alkaline hydrolysis of cyclic esters of propyl phosphonates at different aqueous aprotic solvents

Thermodynamic Function	Thermodynamic functions in various ϕ value						
	Dioxane-H_2O						
	0.00	0.20	0.30	0.50	0.60	0.70	0.80
$\Delta G^{\ddagger}$ (kcal/mol)	25.3	23.8	25.1	22.5	27.9	27.3	35.5
$\Delta H^{\ddagger}$ (kcal/mol)	16.0	15.0	15.9	14.2	17.7	17.3	22.6
$\Delta S^{\ddagger}$ (Gibbs)	−30.8	−29.0	−30.3	−27.5	−33.6	−33.1	−42.5

Thermodynamic Function	Thermodynamic functions in various ϕ value					
	DMSO-H_2O					
	0.00	0.10	0.25	0.40	0.50	0.65
$\Delta G^{\ddagger}$ (kcal/mol)	25.3	25.5	25.7	26.9	27.5	42.8
$\Delta H^{\ddagger}$ (kcal/mol)	16.0	16.1	16.3	17.7	17.5	27.5
$\Delta S^{\ddagger}$ (Gibbs)	−30.8	−31.0	−31.1	−32.5	−33.1	−50.7

Thermodynamic Function	Thermodynamic functions in various ϕ value						
	Acetone-H_2O						
	0.00	0.20	0.35	0.40	0.50	0.65	0.80
$\Delta G^{\ddagger}$ (kcal/mol)	25.3	24.6	24.9	23.2	24.8	26.9	27.3
$\Delta H^{\ddagger}$ (kcal/mol)	16.0	15.6	15.8	14.7	15.4	17.1	17.3
$\Delta S^{\ddagger}$ (Gibbs)	−30.8	−29.8	−30.0	−28.2	−31.0	−32.3	−32.9

ester with a bulky substituent it is helpful to use the solvent with larger donating ability and higher ϕ value.

A series of thermodynamic functions of alkaline hydrolysis of **1** was evaluated based on the measurement of rate constants in various solvent mixtures at different temperatures. The activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are listed in Table IV.

The experimental data showed that, the activation enthalpy decreased in the order of DMSO–water (16.0–27.5 kcal/mol) > dioxane–water (14.2–22.6 kcal/mol) > acetone–water (14.7–17.3 kcal/mol). The magnitude of the $\Delta S^{\ddagger}$ values ($-27.5 \sim -50.7$ Gibbs) indicate that the hydrolytic reaction proceeds by an AE mechanism.

Isokinetic relationship for the solvent effect of the alkaline hydrolysis of **1** was examined. The approximate linear relationship between the activation enthalpy $\Delta H^{\ddagger}$ (kcal/mol) and the activation entropy $\Delta S^{\ddagger}$ (Gibbs) of compound **1** is shown in Figure 8. It indicates that the mechanism of the hydrolysis of **1** in different solvents are of the same type.

EXPERIMENTALS

Materials and Instruments. 2-*n*-propyl- and 2-iso-propyl-2-oxo-1,3,2-dioxaphosphorinanes were synthesized by method described by us.[23]

Acetone was treated in batches of about two liters with a small amount of concentrated phosphoric acid and immediately distilled. Dioxane and DMSO were purified by fractional distillation under reduced pressure.

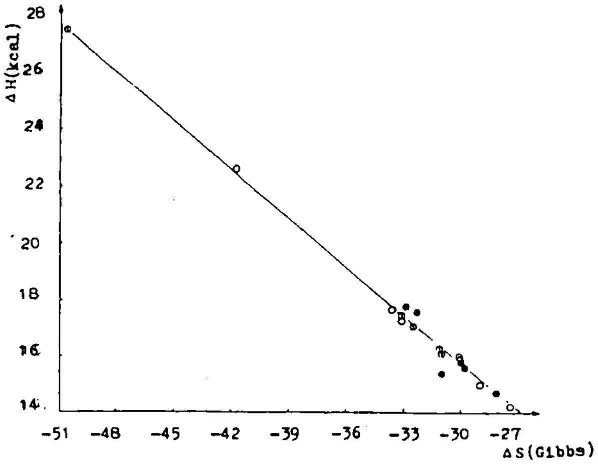

FIGURE 8 Isokinetic relationship of solvent effect on alkaline hydrolysis of **1**
○—in aqueous dioxane, ⦶—in aqueous dimethyl sulfoxide
●—in aqueous acetone

Potentiometric titration was performed on a Metrohm 636-Titroprocessor.

Determination of rate constants. A mixture of solvents with a specified ϕ value containing 0.015 mole cyclic esters of alkylphosphonic acids and sodium hydroxide solution was prepared at room temperature by shaking thoroughly the flask in a Jubalo constant temperature bath (precision ± 0.01°C). At appropriate time intervals, aliquots were removed and followed by addition of standard hydrochloric acid solution to stop the reaction. The excess acid was then back titrated with standard sodium hydroxide solution and the residual concentration of phosphorus ester was estimated. The second order rate constant at various temperature were obtained from both graphical analysis, and a calculation program utilizing the least squares method.

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