KINETICS AND MECHANISM OF THE HYDROLYSIS OF DI-2-PHENYLETHYL PHOSPHATE IN ACID MEDIUM

M. M. MHALA AND V. R. SONAWANE

School of Post-graduate Studies in Chemistry, Jiwaji University, Gwalior

ABSTRACT

Investigation of the hydrolysis of di-2-phenylethyl phosphate in 10% dioxan-water at 98° C in the region 1·0 M to 7·0 M hydrochloric acid shows that it is reactive mainly *via* conjugate acid species. Unlike other substituted alkyl phosphates it shows bend in higher acid region. Ionic strength data shows positive salt effect. Rate coefficients estimated from ionic strength data agree well with the experimental rates. Solvent effect, solvent–isotope effect, Arrhenius parameters and Hammett acidity function have been found to favour unimolecularity of the reaction. Comparative rate data of other esters have been used to discuss the probable reaction paths.

INTRODUCTION

THERE have been very few studies of the kinetics of hydrolysis of simple dialkyl esters. Under all conditions studied, hydrolysis predominantly occurs with the fission of C—O bond. Only dimethyl[1] and dibenzyl[2] phosphates have been studied in detail. In the present investigation, hydrolysis of di-2-phenylethyl phosphate has been studied with a view to know its behaviour in acid region and the results are presented in this paper.

MATERIALS AND METHODS

Di-2-phenylethyl phosphate was prepared by shaking 2-phenylethanol with PCl_5 in the ratio of 3 : 1. In this method triester was also formed. The diester was separated from triester by dissolving it in 10% NaOH solution and then reprecipitated by adding conc. HCl. It was recrystallised from petroleum ether (60–80). M.P. 58° C. (Found C, 62·84% ; H, 6·37% ; P, 9·80% for $C_{16}H_{19}O_4P$. Required C, 62·74% ; H, 6·20%, P, 10·13%).

Deuterium-oxide was obtained from B.A.R.C., Bombay. All the chemicals used were of B.D.H. (A.R.) quality. The kinetic runs were carried out at 98° ± 0·5° C taking 0·0005 M solution of the ester in 10% dioxan water (v/v) mixture. The rate of reaction was determined by colorimetric estimation of inorganic phosphate by Allen's method[3].

RESULT AND DISCUSSION

Pseudo-first order rate coefficients for the hydrolysis of di-2-phenylethyl phosphate in the region 1·0 M to 7·0 M hydrochloric acid show that the rate rises with rise in acidity upto 5·0 M and then decreases. (Table I). The rise in rate with rise in acidity may either be due to incursion of conjugate acid species or to positive ionic strength effect on the hydrolysis *via* neutral species or may be due to both of these effects. Similar maxima have also been observed during hydrolysis of dimethyl[1] and diphenyl[4] phosphates.

TABLE I

Observed and calculated rates of the hydrolysis of di-2-phenylethyl phosphate in acid medium at 98° C

HCl	$10^5 k$ (min.$^{-1}$) (experimental)	$10^5 k$ (min.$^{-1}$) (calculated)
1·0	5·47	5·71
2·0	11·67	10·53
3·0	22·01	25·43
4·0	52·59	58·10
5·0	70·49	69·50 ($n = 1$)
	75·75*	
	88·75**	
	104·00***	
6·0	64·64	62·77 ($n = 3$)
7·0	50·67	42·70 ($n = 4$)

Rates in * 30%, **40% and ***50% dioxan respectively.

Kinetic runs were carried out at constant ionic strength (Table II). At each ionic strength rate increases linearly with the increase in acid concentration. The dependance of rate coefficients on ionic strength is satisfactorily represented by the second emperical term of Debye-Hückel equation[5], $k' = k_0 e^{b\mu}$, where k' and k_0 are respectively the rate constants at any ionic strength and rate at zero ionic strength, b is a constant and μ, ionic strength. At any ionic strength the total rate of hydrolysis, k_e is given by the equation :

$$k_e = k_{N_0} e^{b\mu} + k_{H_0^+} \cdot C_{H^+} \cdot e^{b'\mu}$$

where k_{N_0} and $k_{H_0^+}$ are respectively the rate constants for neutral and conjugate acid species at

TABLE II

Rates of the hydrolysis of di-2-phenylethyl phosphate at constant ionic strength at 98° C

HCl (M)	NaCl (M)	10^3 k (min.$^{-1}$) (experimental)
	$\mu = 1\cdot0$	
0·20	0·80	0·023
0·40	0·60	0·025
0·60	0·40	0·034
0·80	0·20	0·044
	$\mu = 2\cdot0$	
0·20	1·80	0·029
0·50	1·50	0·033
1·50	0·50	0·089
1·80	0·20	0·148
	$\mu = 3\cdot0$	
1·00	2·00	0·084
1·50	1·50	0·123
2·00	1·00	0·158
2·50	0·50	0·189

increases with increase in dioxan content (Table I). The elevation in the rate of hydrolysis may be attributed to the dioxan, a better proton donar[6] in aqueous-dioxan media.

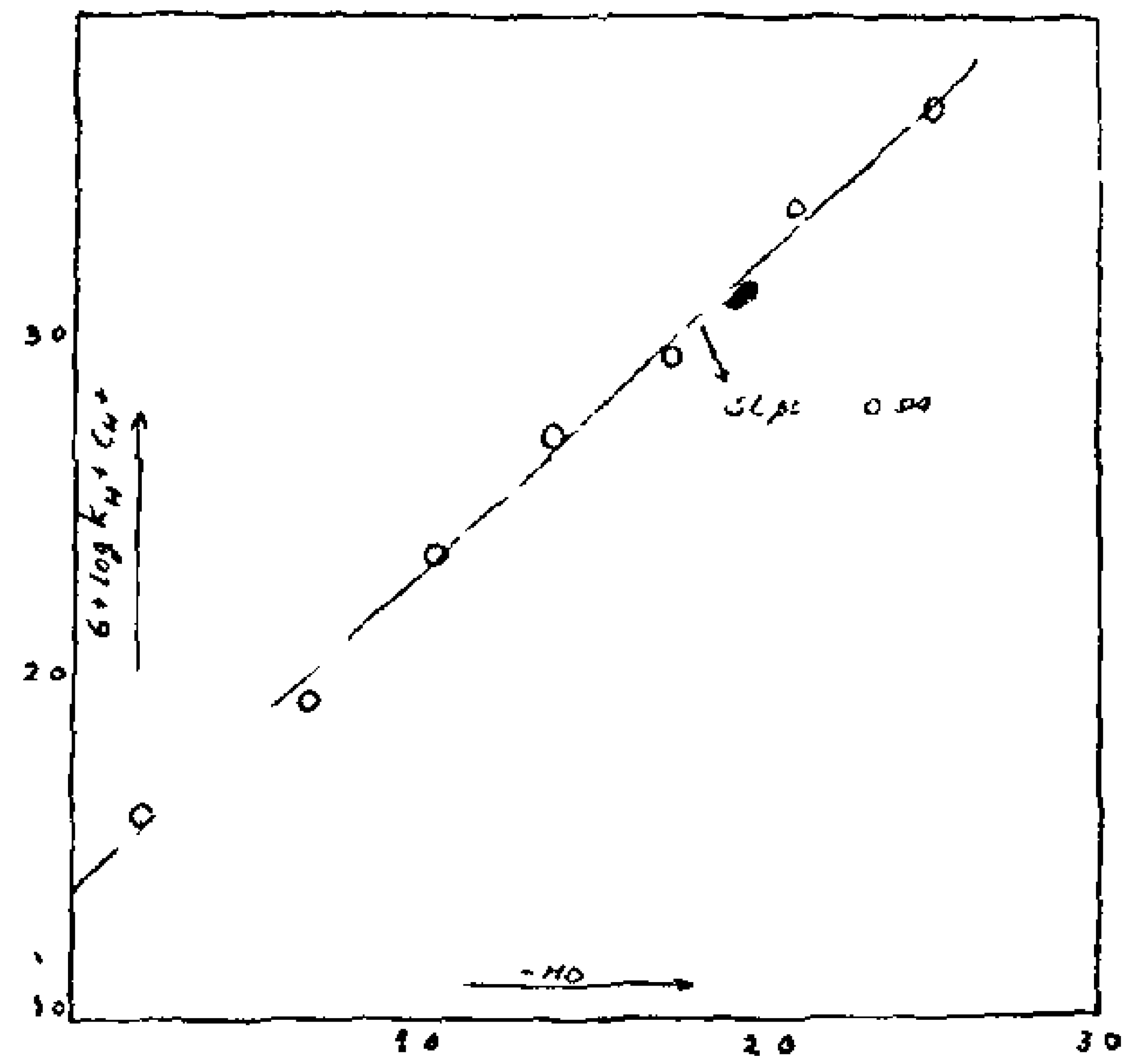


FIG. 1. Hammett plot for the hydrolysis of Di-2-phenylethyle phosphate at 98° C.

Solvent isotope effect in 3·0 M hydrochloric acid (k_{D_2O}/k_{H_2O} = 1·04) favours the formation of conjugate acid species by a fast pre-equilibrium proton transfer[7].

TABLE III

Comparative kinetic rate data for the hydrolysis of diesters via *conjugate acid species*

Phosphates	Temp. °C	E (K.cal/mole)	$\Delta S^{\ddagger}$	Fission	Ref.
Di-allyl-	80	29·30	3·90	C—O	11
Di-*p*-iodo benzyl-	80	24·25	− 9·64	C—O	12
Di-*p*-nitrobenzyl-	80	18·69	−27·99	C—O	13
Di-2-phenylethyl-	98	36·59	17·94	C—O	This work
Di-methyl-	100	..	..	C—O	1

zero ionic strength. The experimentally observed values are : $k_{H_0^+} = 0\cdot15 \times 10^{-5}$ min.$^{-1}$, $k_{N_0} = 1\cdot6 \times 10^{-5}$ min.$^{-1}$, $b = 0\cdot00$ and $b' = 0\cdot25$. Calculated rates from the above equation agree well with the experimentally observed rates (Table I). For the reaction in higher acid media (> 4 M) agreement between the calculated and experimental rates can be sought by water activity and may be represented by the equation :

$$k_e = k_{N_0} \cdot e^{b\mu} + k_{H_0^+} \cdot C_{H^+} \, e^{b'\mu} \, (a\ H_2O)^n$$

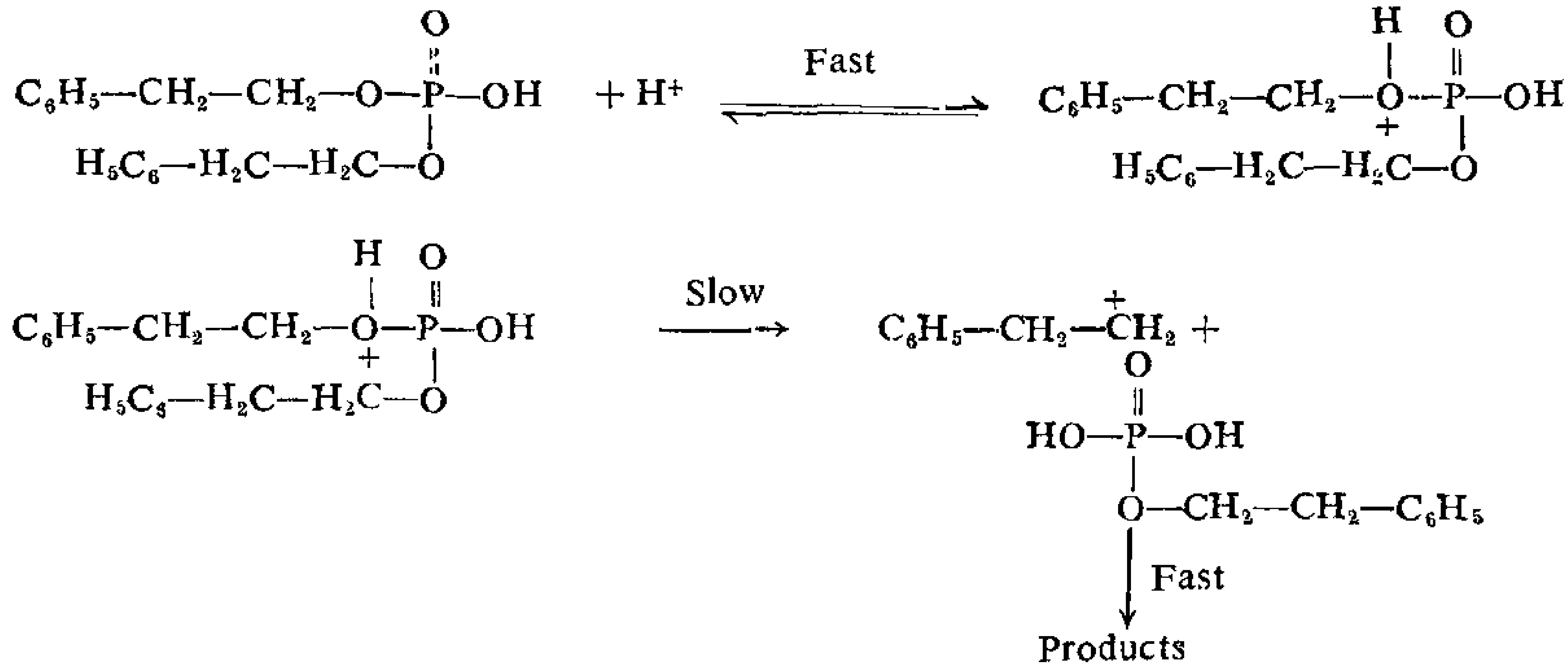
where n is integer whose value increased with the increase in acidity.

Kinetic data of a series of aqueous-dioxan mixtures in 5·0 M HCl at 98° C show that the rate

A plot of log-rate *versus* Hammett acidity function[8] (Fig. 1) shows specific acid catalysed unimolecular hydrolysis of the diester[9]. Arrhenius parameters[10] (E = 36·59 K.cal. mole^{-1}, A = $7\cdot638 \times 10^{17}$ sec.$^{-1}$, $\Delta S^{\ddagger}$ = 17·94 e.u.) in 6·0 M HCl also support the unimolecular nature of the reaction.

Comparative kinetic rate data of other diesters (Table III) of known mechanism support unimolecular hydrolysis of di-2-phenylethyl phosphate *via* C—O bond fission.

In light of the above results the mechanism of the acid hydrolysis of di-2-phenylethyl phosphate may be formulated as :



1. Bunton, C. A., Mhala, M. M., Oldham, K. G. and Vernon, C. A., *J. Chem. Soc.*, 1960, p. 3293.
2. Kumamoto, J. and Westheimer, F. H., *J. Am. Chem. Soc.*, 1955, 77, 2515.
3. Allen, R. J. L., *Biochem. J.*, 1940, 34, 858.
4. Barnard, P. W. C., Bunton, C. A., Kellarman, D., Mhala, M. M., Silver, B. L., Vernon, C. A. and Welch, V. A., *J. Chem. Soc.*, B, 1966, p. 227.
5. Long, F. A. and McDevit, W. F., *Chem Rev.*, 1952, 51, 119.
6. Chanley, J. D. and Feageson, E., *J. Am. Chem. Soc.*, 1958, 80, 2686.
7. Bell, R. P., *Acid Base Catalysis*, Clarendon Press, Oxford, 1949, p. 145.
8. Hammett, L. P., *Physical Organic Chemistry*, McGraw-Hill Book Co., London, 1940, p. 273.
9. Long, F. A. and Paul, M. A., *Chem. Rev.*, 1957, 57, 1.
10. Schalegar, L. L. and Long, F. A., *Advances in Physical Organic Chemistry*, Edited by V. Gold, Academic Press, Inc., London, 1963, Vol. 1.
11. Mhala, M. M. and Saxena, S. B., *Indian J. Chem.*, 1972, 10, 704.
12. Killedar, A. V., *Ph.D. Thesis*, Jiwaji University, Gwalior, 1972.
13. Kavdikar, V. M., *Ibid.*, Jiwaji University, Gwalior, 1970.

SCIENCE ACADEMY MEDALS FOR YOUNG SCIENTISTS, 1978

These medals are awarded annually by the INSA in recognition of outstanding work of scientists below the age of 30 (as reckoned on 31st December preceding the year of award). With the medal there is a cash price of Rs. 1,500/–. In addition, a research grant of Rs. 5,000/– is provided by the Kothari Scientific and Research Institute, Calcutta. Nominations may be made by Fellows of the Academy, as also by Scientific Societies, University Faculties and Departments, and Research Institutions. Members of Sectional Committees of the Academy should not sponsor candidates for the award. The last date for the receipt of nominations is January 31, 1978. Further information and nomination forms may be obtained from the Indian National Science Academy, Bahadur Shah Zafar Marg, New Delhi 110 002, by sending a self-addressed envelope 28 cm × 12 cm.