

STUDY OF SOLVENT EFFECTS ON THE ACIDIC HYDROLYSIS OF MONO-N-ETHYL-*o*-TOLUIDINE PHOSPHATE

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The kinetics of the acid-catalyzed hydrolysis of mono-N-ethyl-*o*-toluidine phosphate was studied in dioxane and dimethyl sulfoxide-water mixtures of varying compositions 0-40% (v/v). The rate coefficients were determined from the rate of appearance of inorganic phosphate, spectrophotometrically by Allen's modified method. Pseudo first order rate coefficients were obtained. The rate of reaction increases with increasing proportion of dioxane and dimethyl sulfoxide at 40, 50 and 60°C. The activation parameters (E_a , ΔH^\ddagger , ΔG^\ddagger , $-\Delta S^\ddagger$) have been evaluated and variations of these parameters have been explained on the basis of solvent-solute interaction, solvent of the transition state of the medium.

KEYWORDS : Mono-N-ethyl-*o*-toluidine phosphate, Solvent effects, Solute-solvent interaction, Activation parameters.

INTRODUCTION

Phosphate esters are compounds with interesting biological and pharmacological properties and are widely used as drugs, nerve gases and pesticides [1]. Phosphate mono and diesters are relatively stable and have important contribution in biochemical reactions [2]. Solvent effect plays significant role in determining chemical reactivity. The rate of an elementary chemical reaction may change by order of magnitude when the solvent is changed [3, 4]. A change in solvent from a polar solvent to a nonpolar solvent has been suggested to increase or decrease reaction rates depending on the type of reactions [5]. The structure of the solvent deciding the hydrogen bonding ability and other solvating interaction plays a vital role in the solvation process [6]. The solvation process is important for understanding the solvent effects on chemical reactions [7].

EXPERIMENTAL

Mono-N-ethyl-*o*-toluidine phosphate (Ba-Salt) has been synthesized by Cavalier method [8] in our laboratory. All the chemicals used were of AR grade and all solutions were prepared in triply distilled water. Hydrolysis of mono-N-ethyl-*o*-toluidine phosphate was carried at various compositions (0 to 40% v/v) of dioxane and dimethyl sulfoxide at 40, 50 and 60°C. Progress of the kinetic reactions was studied by Allen's modified method [9] using spectrophotometer at 735 nm. Pseudo-first order rate constants were determined from first order rate equation.

RESULTS AND DISCUSSION

The kinetics of the hydrolysis of mono-N-ethyl-*o*-toluidine phosphate was studied in 4 mol dm⁻³ HCl at 40, 50 and 60°C. Pseudo-first order rate constants have been obtained and summarized in Table-1. It was found that the rate constant increases with increase in percentage of dioxane and dimethyl sulfoxide from 0 to 40% (v/v) at all temperatures.

Table 1. Kinetic rate data for the hydrolysis of mono-N-ethyl-*o*-toluidine phosphate at different temperatures and solvent mixtures

Solvent % (v/v)	$k \times 10^3 \text{ (min}^{-1}\text{)}$					
	Dioxane			DMSO		
	40°C	50°C	60°C	40°C	50°C	60°C
0	51.32	96.76	184.47	61.58	104.87	195.20
10	59.07	103.72	193.68	71.98	113.29	204.67
20	66.11	109.27	201.27	80.11	122.08	216.12
30	74.23	118.35	209.35	89.01	128.91	225.13
40	84.28	126.24	218.22	97.24	141.54	238.92

Table-2 Activation parameters for the hydrolysis of mono-N-ethyl-*o*-toluidine phosphate

(% v/v)	Dioxane				DMSO			
	E_a	ΔH^\ddagger	ΔG^\ddagger	$-\Delta S^\ddagger$	E_a	ΔH^\ddagger	ΔG^\ddagger	$-\Delta S^\ddagger$
0	55.53	52.88	80.59	85.78	49.78	47.13	85.60	119.09
10	51.70	49.05	85.66	113.35	44.04	41.39	85.61	136.90
20	47.87	45.22	85.60	125.03	42.12	39.47	85.61	142.84
30	44.04	41.39	85.61	136.90	40.21	37.56	85.61	148.77
40	42.12	39.47	85.61	142.84	38.29	35.64	85.53	154.71

$E_a, \Delta H^\ddagger, \Delta G^\ddagger$, in kJ mol⁻¹ and ΔS^\ddagger , in JK⁻¹ mol⁻¹.

From the Table-1 it can be seen that the rate constant values are gradually increasing with the increase in percentage of 1, 4-dioxane and dimethylsulfoxide (DMSO). Dioxane is a polar aprotic solvent while dimethylsulfoxide is a dipolar aprotic solvent. Protic solvents are strong hydrogen-bond donors whereas dipolar aprotic solvents are not. Protic solvents will interact strongly with solutes which are strong hydrogen-bond acceptors. Many dipolar aprotic solvents *e.g.* DMF & DMSO are powerful bases and hydrogen-bond acceptors, so that they have strong interactions with solutes which are strong hydrogen-bond donors [10]. The increasing rate constants values with addition of solvents are required to be discussed on the basis of Hughes and Ingold [11, 12] theory according to which an increase in the dielectric constant values of the reaction media causes an increase in the rate when there is concentration or construction of charges on the transition state and causes a decrease in the rate when there is diffusion or destruction of charges on the transition state. The values of dielectric constants of the reaction media go on increasing with gradual addition of solvent. The results obtained in the present study are in full agreement with the qualitative theory of Hughes and Ingold.

The solvents dioxane and dimethyl sulfoxide showed greater accelerating effect on rate. The variation in the values of rate constant with the alteration in the medium may involve the

interaction of the solvent medium with the reactants, transition states and/or products. The rate of hydrolysis of ester increases when the transition state is better solvated or stabilized by the H-bonding than the initial state [13, 14]. Higher rates are obtained in dimethyl sulfoxide and the lower rates in dioxane as dimethyl sulfoxide has high polarity than dioxane. According to the Parker and Tomilison there is the breakdown of water-water interaction by addition of dimethyl sulfoxide, as a co-solvent in it [15]. This solvent-sheath breaking nature of dimethyl sulfoxide has differential effect on solvent of initial state and of transition state. The rate constants will naturally be affected by such specific solvation changes. As dimethyl sulfoxide is a poor anion solvater there will be decreased in solvation sheath of the anion, OH^- (reactant) with gradual increase in dimethyl sulfoxide proportion in the reaction medium.

Activation parameters are significant in the interpretation of mechanism and provide useful information about the environment in which chemical reactions take place. The activation parameters ΔH^\ddagger , ΔG^\ddagger , $-\Delta S^\ddagger$, exhibit non linear variation with solvent composition for mixed-solvent systems. As shown in Table-2 the values of the entropy of activation ΔS^\ddagger are negative in all solvent mixtures investigated which indicates that the polar transition state is preferentially solvated by water molecules in all of these solvent mixtures. The high values of free energy of activation and enthalpy of activation suggests that the transition state is highly solvated [16].

CONCLUSIONS

The rate of reaction increases with increase in percentage of 1, 4-dioxane and DMSO from 0 to 40 % (v/v) in binary aqueous mixtures at 4.0 mol dm^{-3} HCl. The possible factors influencing the rate are solute-solvent interaction, solvation changes of reactant and transition state. Highest rates are obtained in DMSO and lowest rates are found in 1, 4-dioxane. The activation parameters ΔH^\ddagger , ΔG^\ddagger , $-\Delta S^\ddagger$, exhibit non linear variation with solvent compositions for mixed solvent system.

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REFERENCES

1. Peris-john, R. J., Wickremasinghe, R., *Med. And Hyg.*, **102**, 239 (2008).
2. Cox, J. R., Ramsay, O. B., *Chem. Rev.*, **64**, 317 (1964).
3. Schmeer, G., Six, C., Steinkirchner, J., *J. Sol. Chem.*, **28**, 211 (1999).
4. Bhoite, S. A., Choure, N., *J. Indian Chem. Soc.*, **86**, 1335-1337 (2009).
5. Parker, A., *J. Chem. Rev.*, **69**, 1 (1969).
6. Kemelet, M. J., Abboud, J-L. M., Taft, R. W., *J. Org. Chem.*, **48**, 2887 (1983).
7. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; VCH: (2004).
8. Cavalier, J., *Bull. Soc. Chem. (France)*, **13**, 885 (1895).
9. Allen, R. J. L., The estimation of phosphorus, *Biochem. J.*, **34**, 858-865 (1940).
10. Parker, A. J., *Quart. Rev. London*, **16**, 163 (1962).
11. Ingold, C. K., Hughes, "Structure and Mechanism in Organic Chemistry", *Bell and Sons, London*, **310**, **3**, 45 (1953).
12. Hughes, E. D., Ingold, C. K., *J. Chem. Soc.*, 255 (1935).
13. Cuccovia, I. M., Schroter, E. H., Monteiro, P. M., Chaimovich, H., *J. Org. Chem.*, **43**, 2248-2252 (1978).

14. Al-Shamary, M. N., Al-Lohendan, H. A., Rafiquee, M. Z. A., El-Ablack, F., Zuheir A. Issa, *J. Saudi Chem. Soc.*, **XXX**, 1-9 (2014).
15. Parker, K. J., Tomilison, D. S., *Trans. Faraday Soc.*, **67**, 1301 (1971).
16. Bairagi, B., Bhoite, S. A., Singh, A. K., *Colloid Journal*, **76 (6)**, 765-773 (2014).

