



Study of Solvent Effects on Hydrolysis of Mono-*m*-toluidine Phosphate

Nisha Chhetri, S. A. Bhoite*

School of Studies in Chemistry, Pt. Ravishankar Shukla University,
Raipur-492010, Chhattisgarh, India

Abstract: The study of solvent effects on the hydrolysis of mono-*m*-toluidine phosphate has been carried out in 1, 4 dioxane/water and DMSO/water binary systems at various compositions. The pseudo first order rate constants have been determined. The rate of reaction increases with increase in percentage of 1, 4 dioxane and DMSO from 10 to 50% (v/v) at different temperatures. The activation parameters (ΔH^\ddagger , ΔG^\ddagger , ΔS^\ddagger) have been calculated. The results obtained have been explained on the basis of solute-solvent interaction, solvent of the transition state of the medium.

Keywords: Hydrolysis, Solvent effects, Mono-*m*-toluidine phosphate, Solvent-solute interaction, Activation parameters.

Introduction

Organophosphate esters are the derivatives of orthophosphoric acid. They have found a broad range of applications in the areas of industrial, agricultural and medicinal chemistry owing to their biological and physical properties, as well as their utility as synthetic intermediates¹⁻⁴. Phosphate esters have a unique range of properties which are exploited in the production of specialised chemical processing aids for industry. Solvent effects play a key role in many chemical and physical processes in solutions⁵. The rate of an elementary chemical reaction may change by order of magnitude when the solvent is changed^{6, 7}. 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 reactions⁸. In homogeneous media, solvent effects on reactivity are explained in terms of the specific interactions between solvent and substrate molecules and between solvent and transition states⁹.

Experimental

Mono-*m*-toluidine phosphate was synthesized by Cavalier method¹⁰. It involves the reaction of *m*-toluidine with phosphorylating agent phosphorus pentoxide (P_2O_5) in 1:1 mole ratio. The crude product so obtained was recrystallized by barium hydroxide solution and glacial acetic acid to get pure sample. The confirmation of compound was done by comparing observed and calculated percentage of elements and by recording IR spectrum as shown below :

1. Elemental analysis (%); observed (calculated): C, 26.8 (26.1); H, 2.14 (2.51); N, 4.86 (4.35); P, 9.92 (9.61).
2. IR absorption spectra: The spectrum of mono-*m*-toluidine phosphate was recorded by FTIR. U (KBr) (cm^{-1}): 3100 (N-H); 3125 (O-H); 2945.30 (C-H); 1531.48 (C=C); 1235(P=O); 717.52 (P-N), 974.05 (C-N).

Hydrolysis of mono-*m*-toluidine phosphate ester was carried out at 5.0×10^{-4} mol dm⁻³ in dioxane-water and dimethyl sulfoxide-water medium at various compositions (10-50%, v/v) at 50, 60, 70 and 80°C. The hydrolysis of mono-*m*-toluidine phosphate was studied by spectrophotometric estimation of inorganic phosphate, using Allen's modified method¹¹. All the chemicals used were of A. R. grade.

Results and Discussion

The hydrolysis of mono-*m*-toluidine phosphate has been studied in 1, 4-dioxane-water and DMSO-water binary systems. The rate of reaction increases with increase in percentage of 1, 4-dioxane and dimethylsulfoxide from 10 to 50 % (v/v) in binary aqueous mixtures at various temperatures (50^o, 60^o, 70^o, 80^oC). Pseudo-first-order rate constants have been obtained which are summarized in Table 1.

Table (1): Kinetic rate data for the hydrolysis of mono-*m*-toluidine phosphate at different temperatures and solvent compositions

Solvent % (v/v)	$k \times 10^3$ (min ⁻¹)							
	Dioxane				DMSO			
	50°C	60°C	70°C	80°C	50°C	60°C	70°C	80°C
10	14.2	26.0	53.3	104.6	17.8	32.5	62.3	118.3
20	16.2	29.9	57.4	112.0	22.5	39.8	76.4	138.8
30	19.3	33.2	61.7	120.9	28.8	49.5	92.8	162.2
40	22.3	41.4	77.8	134.4	33.5	60.3	113.2	190.5
50	26.5	47.2	84.9	154.7	40.8	71.2	131.2	222.5

It can be seen from the result that the rate constant values are gradually increasing with increase in percentage of 1, 4-dioxane and dimethylsulfoxide (DMSO). Dioxane is regarded as polar aprotic solvent while dimethylsulfoxide is regarded as 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 donors¹². The increasing trend in the values of rate constants need to be discussed in the light of Hughes and Ingold¹³ predictions 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 percentage compositions of solvent. The results obtained in the present study are in full agreement with the qualitative theory of Hughes and Ingold.

The solvents 1, 4-dioxane and dimethylsulfoxide exerted greater accelerating effect on rate. Intermolecular association of this solvent occurs in such type of binary mixtures. The possible factors influencing the rate are solute-solvent interaction and the solvation changes of reactant and transition state. Highest rates are obtained in dimethylsulfoxide and the lowest rates are found in 1, 4-dioxane because dimethylsulfoxide has high polarity than 1, 4-dioxane. Parker and Tomilison have pointed out the breakdown of water-water interaction by addition of dimethylsulfoxide, as a co-solvent in it¹⁴. The solvent-sheath breaking nature of dimethylsulfoxide 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 dimethylsulfoxide is a poor anion solvater there will be decrease in solvation sheath of the anion, OH⁻ (reactant) with gradual increase in dimethylsulfoxide proportion in the reaction medium.

The activation parameters ΔH^\ddagger , ΔG^\ddagger , ΔS^\ddagger exhibit non linear variation with solvent composition for mixed solvent systems. The calculated values of activation parameters are 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 solvated¹⁵.

Table (2): Activation parameters for the hydrolysis of mono-*m*-toluidine phosphate

% (v/v)	Dioxane			DMSO		
	ΔH^\ddagger	ΔG^\ddagger	$-\Delta S^\ddagger$	ΔH^\ddagger	ΔG^\ddagger	$-\Delta S^\ddagger$
10	14.36	21.69	22.69	13.63	21.54	24.49
20	13.95	21.61	23.70	13.22	21.40	25.32
30	13.08	21.49	26.04	12.65	21.24	26.60
40	12.62	21.40	27.17	12.47	21.14	26.83
50	12.17	21.29	28.25	12.10	21.01	27.60

ΔH^\ddagger , ΔG^\ddagger , in kJ mol^{-1} and ΔS^\ddagger , in $\text{JK}^{-1} \text{mol}^{-1}$.

Conclusion

The rate of reaction increases with increase in percentage of 1, 4-dioxane and DMSO from 10 to 50 % (v/v) in binary aqueous solutions at various temperatures at 4.0 mol dm^{-3} HCl. The main factors involved in the kinetic solvent study are solute-solvent interaction and 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 simple variation with solvent compositions for mixed solvent system. The ΔH^\ddagger and ΔG^\ddagger value decreases with increase of 1, 4-dioxane and DMSO-water mixtures.

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