

Comparative study of effect of some aprotic solvents kinetically on alkalicatalysed hydrolysis of methylsalicylate

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ABSTRACT: Methylsalicylate has been hydrolysed by alkali in aqueous DMSO and aqueous acetone medium at temperatures ranging from 20 to 35°C at various compositions of solvent mixture from 20% (v/v) to 60% (v/v). The specific rate constant was found to decrease with increasing composition of both solvents and prediction of parker was not supported. Variation of other activation parameters ΔH^* , ΔS^* , ΔG^* are also evaluated which have been found to reveal the solvation mechanism by the medium.

Keywords : Solvation, Activation Parameters, Methyl Salicylate, Solvent effect, Aprotic solvents

I. INTRODUCTION

The effect of solvent on alkaline hydrolysis of esters have received continued attention from time to time but explanations put forward are not satisfactory. Hydrolysis of ester is considered as ion-dipole type and assuming the predominance of electrostatic effect, Ingold¹ as well as Laidler and Landskroener² predicted a fall in rate with decreasing dielectric constant of the

medium. However, on the basis of solvation phenomenon, parker³ predicted increase in rate in case of hydrolysis of ester in dipolar aprotic solvents. In our case, decrease in rate with DMSO and acetone solvents does not agree with parker predicament. Attention is being made to study the effect of these solvents kinetically and to establish the mechanism of solvation and the effect of dielectric constant.

II. EXPERIMENTAL

All the chemicals used were either of BDH or Merck grades. The solvents DMSO and acetone were purified by known procedure. Double distilled water was used. Standard solution of 0.01M NaOH was made in different solvent mixtures varying from 20 to 60% in water. The procedure is the same as in previous communication⁴.

The specific rate constants determined at different temperatures and at different solvent compositions are shown in table (I) and (II). The reliability of k values were found to be $\pm 0. \times 10^{-2}$

TABLE-I

Specific rate constant (k) for alkaline hydrolysis of methylsalicylate in aquo - DMSO medium ($k \times 10^2 \text{ dm}^2 \text{ mol}^{-1} \text{ min}^{-1}$)

Temperature(°C)	DMSO (vat%)				
	20	30	40	50	60
20	15.51	11.83	10.19	8.15	6.31
25	31.12	25.90	21.52	18.98	14.22
30	59.18	50.82	45.08	36.31	30.62
35	120.81	97.39	90.12	78.70	63.10

TABLE-II : Specific rate constant (k) for alkaline hydrolysis of methylsalicylate in aqua-acetone medium ($k \times 10^2 \text{ dm}^2 \text{ mol}^{-1} \text{ min}^{-1}$)

Temperature($^{\circ}\text{C}$)	DMSO (vat%)				
	20	30	40	50	60
20	16.70	13.30	10.60	9.10	8.40
25	31.80	24.80	20.00	17.30	15.70
30	60.30	49.60	37.80	31.80	27.90
35	116.10	88.10	66.70	60.80	50.70

III. RESULT AND DISCUSSION

The rate constant values are decreasing with progressive addition of DMSO and acetone at all temperatures. The hydrolysis of ester follows B_{AC}^2 mechanism in Ingold terminology. Since, solvents DMSO, acetone have lower dielectric constants than water, the bulk dielectric constants of the medium will be found to decrease and will disfavor the formation of highly polar transition state. The increase of DMSO in aqueous medium

will facilitate the dissolution of ions already solvated by water. Since, the initial and the transition state cannot be equally desolvated, the rate will be affected by such solvation changes. Since, the rate of reaction decreases, so it appears that desolvation phenomenon is more dominant in transition state than initial state. This is seen by observing the increase in activation energy in case of DMSO solvent mixture.

TABLE-III

DMSO (vol%)	20	30	40	50	60
Ec (kcal mol^{-1})	24.85	25.67	26.35	27.32	27.65

But in case of acetone, activation energy value decreases with increasing percentage of acetone. This decrease in activation energy is attributed by the fact that solvation of one of the states (initial or transition state) is more than the other.

TABLE-IV

Acetone (vol%)	20	30	40	50	60
Ec (Kcal mole^{-1})	22.60	22.20	21.70	21.30	21.10

Thermodynamic Activation Parameters

The thermodynamic activation parameters ΔH^* , ΔS^* and ΔG^* were calculated by usual methods. They have been listed in table V and table VI.

TABLE-V : Thermodynamic Activation parameters in aquo-DMSO medium ΔH^* & ΔG^* in kcal mol^{-1} , ΔS^* in cal $\text{mol}^{-1} \text{ deg}^{-1}$

Vol %	ΔH^*	20 $^{\circ}\text{C}$		25 $^{\circ}\text{C}$		30 $^{\circ}\text{C}$		35 $^{\circ}\text{C}$	
		ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
20	24.31	20.62	12.59	20.57	12.55	20.54	12.44	20.45	12.53
30	25.24	20.78	15.21	20.68	15.29	20.63	15.20	20.58	15.11
40	25.87	20.87	17.07	20.79	17.05	20.70	17.05	20.63	17.01
50	26.90	21.00	21.30	20.86	20.24	20.83	20.01	20.71	20.01
60	27.39	21.15	21.30	21.04	21.32	20.94	21.29	20.91	22.67

TABLE –VI : Thermodynamic activation parameters in aquo – acetone medium ΔH^* & ΔG^* in kcal mol^{-1} , ΔS^* in cal $\text{mol}^{-1} \text{ deg}^{-1}$

Vol%	ΔH^*	20 $^{\circ}\text{C}$		25 $^{\circ}\text{C}$		30 $^{\circ}\text{C}$		35 $^{\circ}\text{C}$	
		ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
20	22.00	20.60	5.00	20.60	4.90	20.50	5.00	20.50	5.10
30	21.60	20.70	3.10	20.70	3.10	20.60	3.20	20.60	3.20
40	21.60	20.80	0.70	20.80	0.80	20.80	0.80	20.80	0.80

50	20.90	20.90	-0.3	20.90	-0.20	20.90	-0.20	20.90	-1.20
60	20.60	21.00	-1.3	21.00	-1.20	21.00	-1.3	21.00	-1.20

It is observed that as the proportion of DMSO and acetone in aquo– solvent mixture is increased, the free energy values increase very slowly. This indicates that stability of the transition state is very little affected by addition of organic co-solvents. The increase value of entropy change with increase in the proportion of DMSO solvent indicates about the dominancy of desolvation phenomena of transition state than the initial state. But in case of acetone solvent, entropy values decrease which interprets about the solvation of reactant or transition state dominant. The variation of ΔH^* and ΔS^* gives straight line plot which follows Barchay – Butler rule⁵.

The decrease in ΔS^* values justify that there is greater solvation of transition state compared to the initial state. These may also be explained by Frauk and Evens Concept that the solute molecule in dilute solvent solution builds a structure of considerable number of solvent molecules around itself.

Effect of ionic Stroengh

There is a small influence of ionic stroengh on the reaction rate. This suggests that the reaction is not ion-ion but ion-molecular in nature.

REFERENCES

- [1]. C.K. Ingold, "Structure and Mechanism in Organic Chemistry" Bell, London, 1953
- [2]. K.J. Laidler and P.A. Landskrocner, Trans-Faraday Soc., 1956, 52, 200
- [3]. A.J. Parker, Chem. Rev. 1969, 69,1
- [4]. D.K. Verma, Bhagwanji Singh and Ramprवेश Singh, J. India Chem. Soc. Vol.69, Dec.1992
- [5]. Barclay I.A. and Butler J.A.V., Trans Faraday Soc. 1938, 34, 1945
- [6]. D.D. Roberts, J. Org, Chem. 1965, 30, 3516
- [7]. D.D. Roberts, J. Org, Chem. 1966, 31, 4037
- [8]. P.S. Radlakrishnamurti and P.C. Patra, Tetrahedran 1974, 26, 5503
- [9]. R.C. Jha, L.Singh and S.N. Das, J. IndianChem. Soc. 1974, 51, 657
- [10]. L. Singh, R.T. Singh and R.C. Jha, J. Indian Chem. Soc. 1980, 57, 1089
- [11]. L. Singh, R.T. Singh and R.S. Jha, J.Indian Chem. Soc. 1981, 58, 966
- [12]. S.V. Anantkrishnan and P.S. Radhkrishnamurti, J. IndianChem. Soc. 1965, 3, 886
- [13]. G. Nageshwar Rao and S.B. Ronald, J. Indian Chem. Soc. 2002, 79, 416
- [14]. Kabir-ud-Din, W. Fatma and Zaheer Khan, J. Indian Chem, Soc. 2005, 82, 811
- [15]. D.S. Bhuvaneshwari and K.P. Elange, J. IndianChem. Soc. 2006, 83, 999
- [16]. A.J. Kirty, N.R. Dutta, D.Silva and J.M. Goodma, J. Am. Chem. Soc. 2007, 127, 7033
- [17]. Tauheed Sarwat, Haidler S.R. and Singh R.T., A.R.J. Phys. Sc. **10**, 2007, No(1-2), 201-204
- [18]. Upadhaye, M.K. Kumar, A. Singh, V.K. and Singh R.T., A.R.J. Phys.Sc.,**11**, 2008, No (1-2), 133-138
- [19]. H. Singh, O.P. Prasad, R.Ojha and R.T. Singh, MRJ Sci. 2016, 20, 65-77