Specific-Base Catalysed Hydrolysis of Methyl Salicylate and Isoamyl Salicylate in Water-Ethanol Binary Solvent System

BIHARI SINGH†, SANT KISHORE PRASAD* and RAJIV RANJAN
Department of Chemistry
S.S.J.S.N. College, Garhwa-822 114, India

Methyl salicylate and isoamyl salicylate have been hydrolysed in presence of hydroxide anion as catalyst in water-ethanol solvent mixtures at varying composition and temperature. Variations in specific rate constant and dielectric constant values have been determined at all the temperatures and the composition of organic co-solvent used. The thermodynamic activation parameters have also been evaluated using the experimental data. A reasonable interpretation of the experimental data has been given on the basis of solvent-solute interactions, solvation of the transition state and the dielectric behaviour of the medium.

INTRODUCTION

Review of literature[1-6] relating to the effect of solvent on ion-dipole type of reaction reveals interesting and in some cases contradictory results regarding the interaction of solvent molecules with reacting species in it. Roberts[7, 8] supported the view of Parker[9] which predicts increasing rate in case of ester hydrolysis in aquo-dipolar aprotic solvent mixtures. However, the studies of other workers[1-6, 10] reveal that results are not in line with that of Parker. They support the view of Ingold[11] and of Laidler[1] who predicted the decrease in the rate with decreasing dielectric constant of the media. In few cases[12], Parker's views have been found to be operative in lower concentration region of the organic co-solvent but Ingold[11] and Laidler's[1] view has been found to be applicable in the higher concentration region. Obviously more work is still to be done to establish the mechanism of solvation and effect of the dielectric constant of the medium on ion-dipolar type of reactions. In view of the above observations the study of the kinetics of hydroxide anion catalysed hydrolysis of the above mentioned esters in aquo-ethanol solvent mixtures have been undertaken for investigation.

EXPERIMENTAL

Analar and standard grade chemicals (B.D.H., E. Merck) were used. Organic solvent ethanol was purified by following the usual method as described by Perrin *et al*[13]. Methyl salicylate of B.D.H. make was first distilled under reduced pressure which was further purified by repeating the distillation process and the fraction between 221–224°C was collected. The b.p. of the distilled product was found to be 223°C which confirmed its purity. Similarly isoamyl salicylate of BDH make was first distilled under reduced pressure. It was then subjected to fractional distillation under laboratory conditions and the fraction between 274–277°C was collected.

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†Department of Chemistry, A.N. College, Patna-800 013, India.

The b.p. of the distilled product was found to be 276°C (sharp) which confirmed its purity. The standard ester and alkali solutions were prepared in double distilled water free from carbon dioxide. The standard solutions of sodium hydroxide and ester solutions were thermostated separately in a water bath (±0.5°C) for 0.5 h and the solutions were then mixed together. 10 mL of this reaction mixture withdrawn at definite intervals of time was poured into an ice-cold standard 10 mL, 0.1 N HCl solution and titrated against standard baryta solution. Reproducible results were obtained. The specific rate constant (k) values calculated in various solvent compositions at different temperature are given in Table-1.

TABLE-1

SPECIFIC RATE CONSTANT ($k \times 10^2$ in lit mol^{-1} min^{-1}) OF METHYL AND ISOAMYL SALICYLATES IN WATER-ETHANOL BINARY SOLVENT SYSTEM

Temp. (°C)	Ester	Ethanol % (v/v)					
		10	20	30	40	50	70
20	Methyl salicylate	22.80	18.16	14.16	12.58	10.64	9.35
	Isoamyl salicylate	14.99	12.06	10.07	7.89	7.04	5.55
25	Methyl salicylate	33.18	31.12	25.29	22.80	19.32	16.33
	Isoamyl salicylate	23.13	20.81	18.11	15.15	12.70	11.46
30	Methyl salicylate	55.33	44.26	40.15	32.43	29.24	25.29
	Isoamyl salicylate	38.90	32.28	28.99	25.81	22.00	20.85
35	Methyl salicylate	97.27	69.82	67.76	56.52	49.09	41.50.
	Isoamyl salicylate	71.10	56.49	51.89	46.78	41.74	33.58

RESULTS AND DISCUSSION

Rate constant values ($k \times 10^2$) for both the esters gradually decrease with increasing proportion of ethanol at all the temperatures as shown in Table-1. The hydrolysis of the esters follows the second order kinetics. The observed decrease in the rate constant is the overall effect of decrease in the bulk dielectric constant value of the medium and disfavouring the formation of the transition state. This is what has been our observation in case of both the esters. It is supported by theory of Hughes[14] and Ingold[11] and also from the prediction of Laidler and Landskroener[1] and Fradenbagen[15].

Variation of rate constant against mole per cent of ethanol

A peculiar feature of variation has been noted by plotting log k *vs.* mole per cent of ethanol (Figs. 1 and 2). At lower mole per cent of ethanol, the decrease in log k values for both the esters is sharp but they approach a limiting value in the region of 30–40 mole per cent of ethanol.

Effect of temperature and activation energy (Ec)

Rate constant (k) values are found to increase with increasing temperature according to the Arrhenius law, yielding a good straight line for log k *vs.* 1/T. The E_C values have been found to increase in both the esters (Table-2) with

increasing volume per cent of ethanol. The gradual increase in E_C values can be explained on the fact that the transition state is more desolvated than the initial state (Figs. 3 and 4).
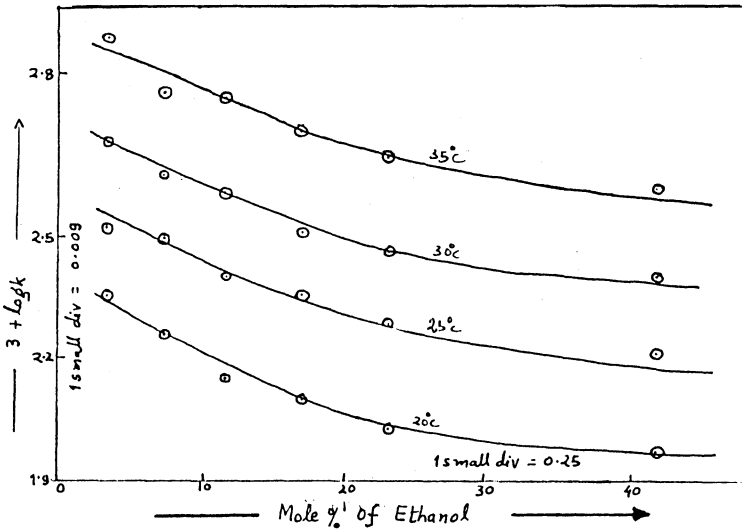

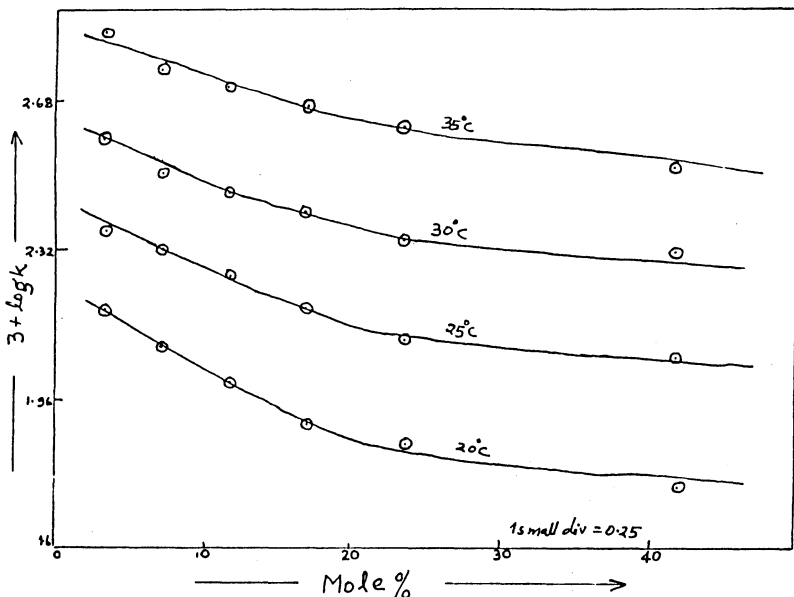Fig. 1. Plot of log k vs. mole % of ethanol for hydroxide anion catalysed solvolysis of methyl salicylate

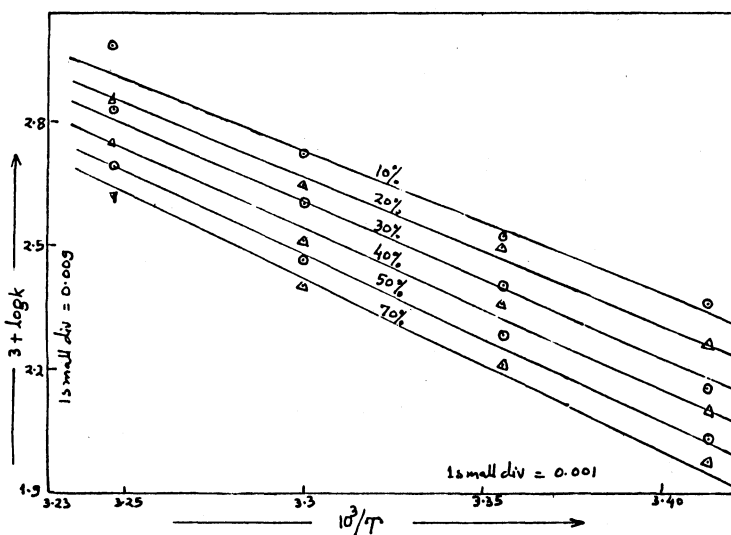Fig. 2. Plot of log k vs. mole % of ethanol for hydroxide anion catalysed solvolysis of isoamyl salicylate

Fig. 3. Plot of log k *vs.* $10^3/T$ for hydroxide anion catalysed solvolysis of methyl salicylate in water-ethanol mixtures

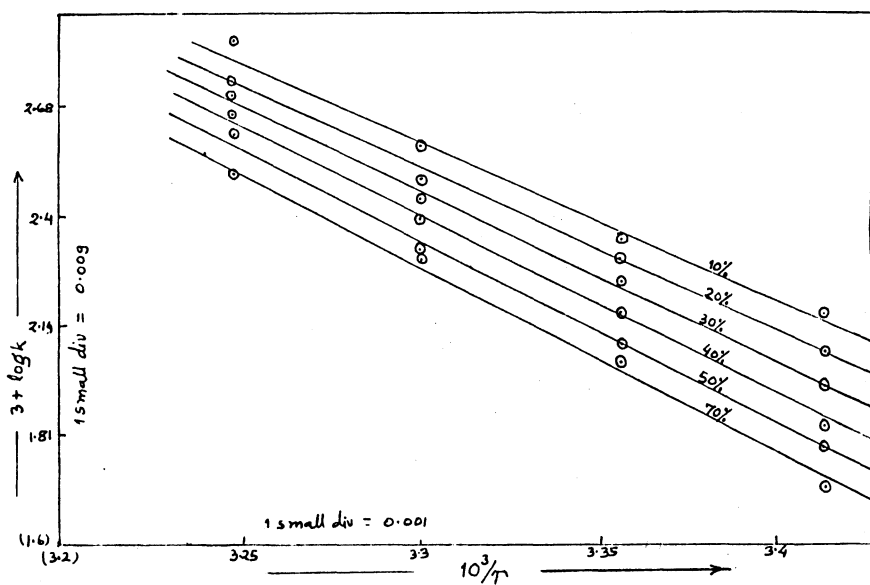
Fig. 4. Plot of log k *vs.* $10^3/T$ for hydroxide anion catalysed solvolysis of isoamyl salicylate in water-ethanol mixtures

TABLE-2
ACTIVATION PARAMETERS OF METHYL AND ISOAMYL SALICYLATE IN
DIFFERENT COMPOSITIONS OF WATER-ETHANOL BINARY SOLVENT SYSTEM

Ester	ethanol (v/v) (%)	E_C (kJ K^{-1} mol^{-1})	ΔH^* (kJ K^{-1} mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔG^* at 35°C (kJ mol^{-1})
Methyl salicylate	10	66.2	63.9	−39.29	76.0
	20	68.9	66.4	−32.0	76.3
	30	72.5	68.9	−25.1	76.7
	40	74.5	72.4	−14.7	76.9
	50	77.3	75.0	−7.5	77.3
	70	80.2	77.7	0.28	77.6
Isoamyl salicylate	10	75.5	72.6	−13.1	76.7
	20	77.2	74.3	−8.8	77.0
	30	80.4	77.6	0.8	77.3
	40	82.9	80.5	9.3	77.6
	50	87.6	83.9	19.7	77.9
	70	88.6	87.3	29.7	78.2

Iso-dielectric activation energy (E_D)

E_D values for both the esters in water-ethanol binary solvent systems at different dielectric constant (D) have been calculated (Table-3). On perusal of the E_D values it is evident that the effect of solvation appears to be small as the change in E_D value is quite small for both the esters.

TABLE-3
ISO DIELECTRIC ACTIVATION ENERGY, E_D, FOR METHYL AND
ISOAMYL SALICYLATE ESTERS AT THE DIFFERENT DIELECTRIC CONSTANT (D)

Methyl salicylate ester					
Dielectric constant value, D	52	54	56	58	60
E_D (kJ mol^{-1})	83.7	82.5	82.1	81.3	80.3

Isoamyl salicylate ester						
D	51	53	55	57	59	61	63
E_D (kJ mol^{-1})	86.4	86.3	85.9	84.4	82.8	82.0	80.6

Other thermodynamic activation parameters

The thermodynamic activation parameters ΔH^*, ΔS^* and ΔG^* were calculated by usual methods (Table-2). The increase in ΔG^*, though small with the increase in ethanol proportion, is indicative of the specific desolvation of the transition state. This is in accordance with our view that the transition state is less solvated or more desolvated than the reactants in initial state. Cleave[16] and Elsemongy[17] got similar observations.

Effect of ionic strength

There is practically no effect of ionic strength on the rate constant. It is, therefore, indicative of the fact that solvolysis of the esters under investigation are of ion-molecular type and not of ion-ion type.

Comparative study of rate constants of methyl and iosamyl salicylates

A comparison of rate constant values of methyl and ethyl salicylates (Table-1) reveals that the value of k decreases when methyl group is substituted by isoamyl group.

Isoamyl group being more bulky than methyl group it is expected that attack of OH⁻ anion on the —COOR part of the ester will be sterically more hindered in case of isoamyl group as compared to methyl group.

ACKNOWLEDGEMENT

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