

Comparative Study of the Kinetics of Base Catalysed Hydrolysis of Iso-Amyl Salicylate in Aquo-Ethylene Glycol, Aquo-n-Propyl Alcohol and Aquo-Tertiary Butyl Alcohol

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Kinetic studies of the base catalysed hydrolysis of iso-amyl salicylate in aqueous ethylene glycol, aqueous n-propyl alcohol and aqueous tertiary butyl alcohol medium at various compositions starting from 10 to 40% (volume %) ethylene glycol, n-propyl alcohol and tertiary butyl alcohol respectively at temperatures ranging from 15 to 35°C are reported. The specific rate constant values were found to decrease with increasing proportion of co-solvents at all the temperatures and the prediction of Parker is not supported. Both iso-composition activation energy E_C and isodi-electric activation energy E_D values increase with increases in proportion of the organic co-solvents. Variation in other thermodynamic parameters such as ΔS^* , ΔH^* and ΔG^* are also evaluated and interpreted on the basis of solvation concept.

INTRODUCTION

The solvent effect study on the base catalysed hydrolysis of esters has received continued attention from time to time, but explanations put forward are not satisfactory. According to Laidler¹ and Ingold² rate of alkaline hydrolysis of esters decreases with decreasing dielectric constant of the medium. Hydrolysis is of ion-dipole type and electrostatic effect predominates, for which there is general experimental evidence. The decrease in rate of hydrolysis of esters upon addition of co-solvents (organic solvent) has been observed by other workers also.³⁻⁵ But more works are needed to establish the mechanism of solvation and the effect of dielectric constant with variation with regard to the various co-organic solvents. Among the esters studied thoroughly so far, the substituted esters of benzoic acid appear to have received very little attention. Therefore, it is thought worthwhile to study the effect of solvent such as ethylene glycol, n-propyl alcohol and tertiary butyl alcohol on the rate as well as the various thermodynamic parameters in base catalysed hydrolysis of iso-amyl salicylate at different temperatures and composition to arrive at some definite conclusions. Further, this may provide some interesting information on account of charge localization on the ester molecules.

EXPERIMENTAL

All the required chemicals used were of BDH/E. Merck grade. Ethylene glycol, n-propyl alcohol and tertiary butyl alcohol were purified by standard methods. Double distilled water free from CO₂ was used. Iso-amyl salicylate was also purified by fractional distillation method under laboratory conditions. The boiling point of the distilled product was found to be 276°C (sharp) which confirmed its purity. Standard solutions of NaOH (0.2 N) and iso-amyl salicylate (M/6) were made. Varying compositions of organic co-solvents in water were 10 to 40%. 10 mL of M/6 ester was added to the reaction mixture which was thermostated for $\frac{1}{2}$ h 10 mL of this reaction mixture was removed and mixed with content of 20–25 mL ice-cold water and 10 mL of standard HCl kept in a clean conical flask and finally titrated with standard baryta solution. Remarkable results were obtained in these studies. The specific rate constants (K) were determined at temperatures varying from 15 to 35°C at intervals of 5°C for various compositions of aquo-organic solvents and are shown in Table-1.

TABLE-1
SPECIFIC RATE CONSTANTS (K) FOR ALKALINE HYDROLYSIS OF ISO-AMYL SALICYLATE IN AQUO-ETHYLENE GLYCOL, AQUO-N-PROPYL ALCOHOL AND AQUO-TERTIARY BUTYL ALCOHOL

(K × 10¹ in dm³ mole⁻¹ min⁻¹)

Temp. in °C	Ethylene glycol (vol %)				n-Propyl alcohol (vol %)				Tertiary butyl alcohol (vol %)			
	10	20	30	40	10	20	30	40	10	20	30	40
15	5.8	4.9	3.7	2.8	—	—	—	—	—	—	—	—
20	8.7	7.5	6.0	4.8	—	—	—	—	—	—	—	—
25	12.6	11.5	9.5	8.5	1.81	1.72	1.61	1.52	7.1	6.1	5.5	4.5
30	—	—	—	—	3.95	3.84	3.73	3.64	10.3	9.2	8.5	7.5
35	24.9	23.8	22.5	21.5	—	—	—	—	15.0	13.8	12.8	11.5
40	—	—	—	—	5.21	5.12	5.00	4.89	21.6	20.5	19.4	18.5

RESULTS AND DISCUSSION

The trend of change in specific rate constant (K) values is identical in one aspect. It is that with the successive addition of each of the three organic co-solvents the K value goes on decreasing at all the temperatures and in the whole range of solvent composition from 10 to 40% of the organic co-solvent (v/v). Furthermore, for the same ester (*i.e.*, iso-amyl salicylate) and having all other parameters remaining identical, the K values have been found to be in the order (vide Table-1)

Aquo-ethylene glycol > tert. butyl alcohol > n-propyl alcohol.

The observed decrease in the rate with the increasing of the organic co-solvent is the combined effect of both (i) decreasing dielectric constant value of the

medium (D_{298} for pure ethylene glycol, n-propyl alcohol and tert. butyl alcohol are 37.70, 20.33 and approx 20 respectively), and (ii) solvation change in the initial state (*i.e.*, reactants) and the transition state. As has been noted below under activation parameters the increase in ΔS^* value with increase in proportion of the organic co-solvent in the reaction medium suggests that the phenomenon of desolvation is more dominant in the transition state than that in the initial state. Our observations also get qualitative support from Hughes and Ingold theory² and from the predictions of Laidler and Landskroener.¹

Activation parameters: K values are found to increase with increasing temperature in accordance with the Arrhenius equation, yielding good straight lines for plots of $\log K$ vs γ/T . Iso-composition activation energies for different compositions were obtained using these plots. The isodielectric activation energy values E_D were also calculated as reported by Wolford.⁶ It was done to minimize

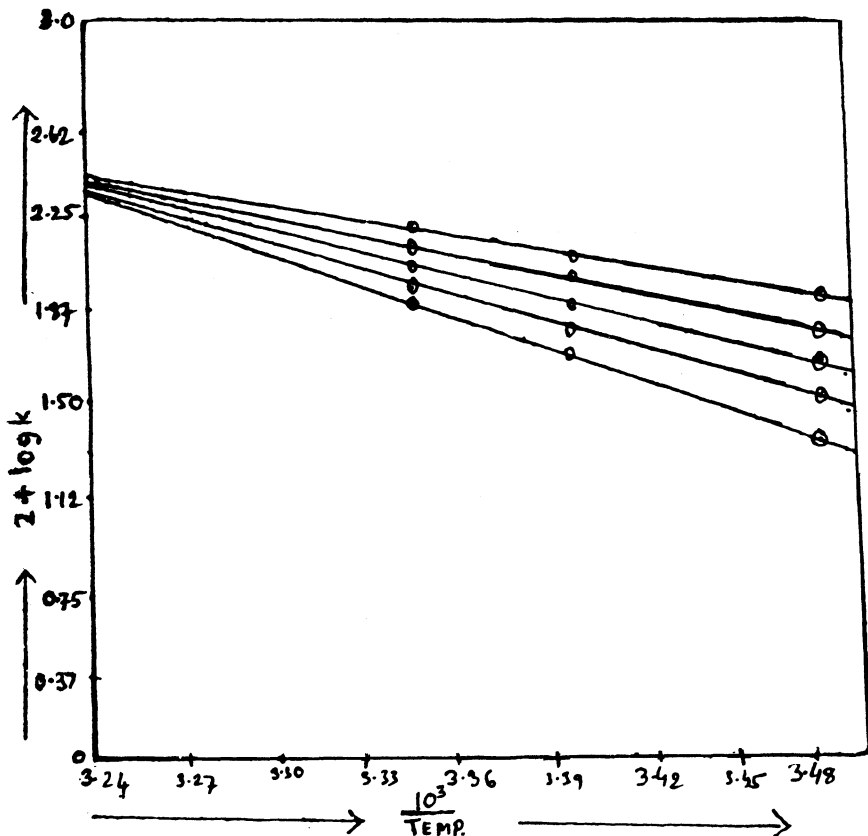


Fig. 1. Plot of $2 + \log K$ vs. $10^3/T$ for alkaline hydrolysis of iso-amyl salicylate in aquo-ethylene glycol

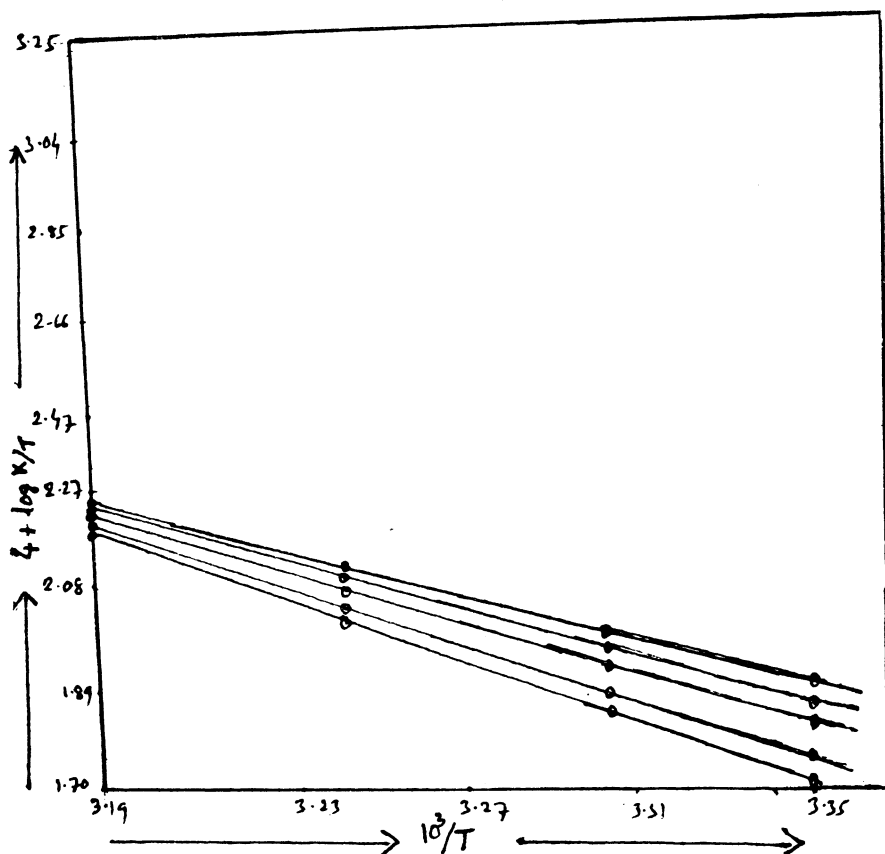


Fig. 2. Plot of $4 + \log K/T$ vs. $10^3/T$ for alkaline hydrolysis of iso-amyl salicylate in aquo-*n*-propyl alcohol medium

the effect of dielectric constant. These values have been reported in Tables 2 and 3.

TABLE-2
ISO-COMPOSITION ACTIVATION ENERGIES (E_c)

Vol %	Ethylene glycol				n-propyl alcohol				Tertiary butyl alcohol			
	10	20	30	40	10	20	30	40	10	20	30	40
E_c (kJ. mol ⁻¹)	52.22	57.44	63.82	72.48	57.44	55.04	58.97	59.83	56.57	61.82	65.56	71.80

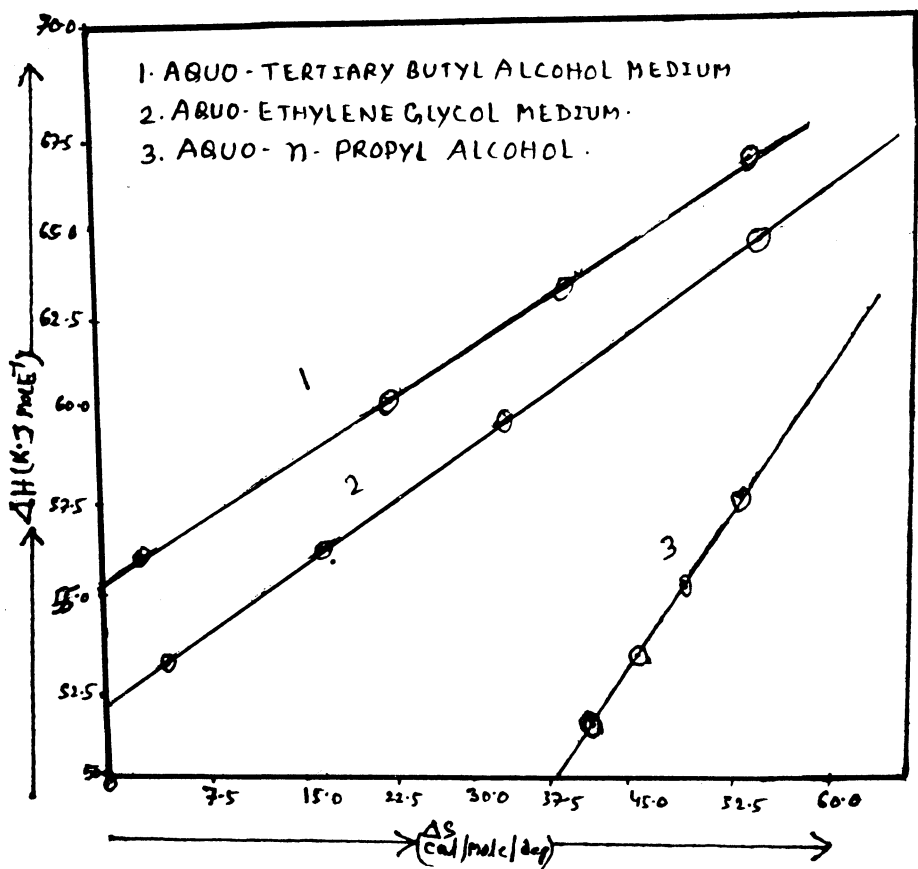


Fig. 3. Plot of ΔH vs. ΔS for alkaline hydrolysis of iso-amyl salicylate in aquo-tertiary butyl alcohol, aquo-ethylene glycol and aquo-n-propyl alcohol medium

TABLE-3
ISO-DIELECTRIC ACTIVATION ENERGIES E_D

Dielectric constant values	Aquo-ethylene glycol					Aquo n-propyl alcohol				Aquo tert. butyl alcohol			
		64	66	68	70	72	54	58	62	66	48	52	56
E_D in (kJ mole ⁻¹)	8.9	8.34	8.32	7.65	7.60	10.41	11.48	11.48	11.29	63.8	65.1	66.6	68.4

Other activation parameters were calculated using Wynne-Jone and Eyring equation¹² in the following form:

$$\log \frac{k}{T} = \left[\log \frac{K}{h} + \frac{\Delta S^*}{2.303R} \right] - \frac{\Delta H^*}{2.303R} \times \frac{1}{T}$$

From the plots of $\log \frac{K}{T}$ against $1/T$, the values of ΔH^* and ΔS^* were obtained.

ΔG^* values were then obtained by using the thermodynamic relation

$$\Delta G^* = \Delta H^* - T \times \Delta S^*$$

The values of ΔH^* , ΔS^* and ΔG^* have been recorded in Table-4.

TABLE-4
ACTIVATION PARAMETERS FOR ALKALINE HYDROLYSIS OF ISO-AMYL SALICYLATE IN AQUO-ETHYLENE GLYCOL, AQUO-n-PROPYL ALCOHOL AND AQUO TERT. BUTYL ALCOHOL

(ΔH^* in kJ mole^{-1} , ΔG^* in kJ mole^{-1} and ΔS^* in $\text{cal. mole}^{-1} \text{ deg}^{-1}$)

Vol %	Ethylene glycol					n-propyl alcohol		
	ΔH^*	15°C ΔG^*	20°C ΔG^*	25°C ΔG^*	25°C ΔS^*	(25°C) ΔH^* ΔG^* ΔS^*		
10	50.32	49.62	49.64	49.57	2.50	51.88	71.27	-239.71
20	54.25	50.12	50.03	49.91	14.53	54.18	71.49	-240.08
30	60.46	50.78	50.32	50.32	34.04	55.71	71.66	-240.66
40	76.01	51.44	51.10	50.60	55.07	58.39	71.82	-241.22

Vol %	Tertiary butyl alcohol				
	ΔH^*	25°C ΔG^*	25°C ΔS^*	30°C ΔG^*	40°C ΔS^*
10	55.27	51.04	13.99	50.99	50.94
20	58.50	51.41	23.84	51.27	51.12
30	62.43	51.09	36.05	51.51	51.36
40	67.37	59.04	57.37	51.80	51.39

Both E_C and E_D values increase with increase in proportion of organic solvent in the reaction medium. The decreasing value of specific rate constants with increasing proportion of organic co-solvent is thus supported.

The increase in ΔG^* though very small is significant. Increase in ΔG^* is a sign of specific desolvation of the transition state. This is in agreement with our views that the transition state is less solvated or desolvated than the initial state with addition of co-organic solvent in mixture. Cleve¹¹ and Elsemngy⁷ have observed a similar increase in ΔG^* .

ΔH^* and ΔS^* values are also showing considerable variation, the increase being quite smooth. Isokinetic relationship between ΔH^* and ΔS^* are obeying Barclay and Butter rule⁹ giving an excellent straight line when ΔH^* is plotted against ΔS^* . The increase in ΔS^* suggests the formation of more mobile transition state which supports contention of desolvation of the transition state.

Effect of ionic strength: There is a small influence of ionic strength on the reaction rate. It is, therefore, indicative of the fact that the hydrolysis reactions under study are not ion-ion type but an ion-dipolar molecule type of reaction.

Similar ion-dipolar molecule type of reactions have been reported by Moelwyn Hughes.¹⁰

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