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Research Article

Activation Parameters and Solvent Effect: A Kinetic Reaction OF Ethyl Caprylate in Water-Acetone Media

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ABSTRACT

The kinetic result of hydrolysis of Ethyl Caprlyate was investigated at different composition of aqueous organic solvent with Acetone (30-70% v/v) over the temperature range of 20 to 400c. The calculated result follows second-order kinetics and observed that the rate decreases with increasing proportion of acetone. This behavior is attributed the electrostatic nature that various solvent-solute interactions occurs in the reaction media. Linear plots of logk with different water concentration show that the equilibrium shifted from dense form to bulky form. Iso-kinetic temperature has been determined with the help of slopes of versus. Thermodynamic parameter was calculated with the help of Wynne-Jones and Eyring equation.

Keywords: Ethyl Caprylate; kinetics solvent effect; Acetone-water; activation parameter

INTRODUCTİON

A large number of investigations are made on studies of solvent effect on hydrolysis of different esters in aqueous binary solvent system [1-5], but there is very little attention put forward on alkali catalised hydrolysis of Ethyl Caprylate. Ethyl caprylate is a fatty acid ethyl ester has prominent role as a metabolite. It is a suitable reagent used as a standard for measurement of flavour-active compounds by gas chromatography. It is also used in brown cocoa, dairy, savory, etc. Predictions of Ingold [6] and Laidlar [7] showed that the rate of reaction is expected to increase with the increase of dielectric constant of the reaction media. However Parker [8] and Roberts [9] found decrease in rate with increase of dielectric constant under similar conditions. Actually solvent- solute interaction and salvation of reactants and transition states are the dominating factors which influence the reaction rate in aqueous solvent system. In this studies, an attempt has to be made to investigate the influence of dipolar aprotic solvent (Acetone) on the reaction of ethyl caprylate in aqueous solvent system at different temperature.

EXPERIMENTAL

The Kinetics of alkali catalyzed hydrolysis of Ethyl Capyrlate ester was studies over different range of temperature (20 to 400c). The entire chemical used was AnalaR or c p Merck. Water used during the experiment is double distilled. Organic solvent are purified by known procedure. Calculated amount of NaOH, water, organic solvent (Acetone) and ester were thermostated. From zero time onward 10 ml of reaction mixture was quickly poured into chilled flask containing 10ml standard hydrochloric acid which is quickly titrated against the barytha solution.

The titer reading was noted with definite interval of time. The calculated rate, using second order reaction is inserted in Table-1.

RESULT AND DISCUSSION

Effect of solvent on hydrolysis rate: The second order rate constant of the reaction in water-Acetone were calculated from linear plots of logk against time. It is obvious from the result obtained in Table-1 that the values of rate decrease with gradual addition of solvent. The decrease in rate is due to precipitation of OH- ion.

The negative charge is believed to be dispersed on large area of the transition state. Hence this result is against the past theory of Haugh and Ingold [6] but in some case it is found similar as result of its case [10, 11]. However it is observed that rate is affected due to change in solvation and dielectric vales simultaneously.

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Table1: Second order rate constant values [k x103(dm) 3/ mole/mint] at different solvent composition.

Temp in OC	% of Acetone				
	30%	40%	50%	60%	70%
20OC	26.91	23.71	21.33	18.48	15.84
25OC	55.59	46.66	39.81	33.11	26.30
30OC	107.15	89.12	72.44	58.74	42.65
35OC	208.92	164.05	127.35	100.00	67.60
40OC	398.10	305.49	229.08	175.79	107.15

Mechanistic path ways and role of water molecule:

The slope [Table-3, fig-1] of plots of logk values with different water concentration, the number of water molecule involve in transition state was determined as suggested by Tommila[12] and Lane[13]. The rate governing step of Ethyl Caprylate consist of attack of hydroxyl ion on carbonyl and water moluclе on ester oxygen simultaneously as suggested by Laidler and Landskskroer[7]. The plots of logk verses log [H2O] were found to be 1.16 to 2.34 with increasing temperature [Table-3]. This result shows that the nearly1.16 to 2.34 water molecule take part in formation of activated complex with increase of temperature.

Robertson [14] proposed a relation

$$\mathrm{log}k = \mathrm{log}k0 + n\ \mathrm{log}[H2O]$$

Where n is the salvation number (n) which is determined by plotting logk against log [H2O]. The salvation number help us to decide the criterion for studies of mechanism of the reaction in aqueous solvent system.. From the values of water molecules associated with transition state, it may be inferred that structure of water in water-acetone media changes from dense form to bulky form with increase the temperature of reaction.

$$[H2O]\ d \leftrightarrow [H2O]\ b$$

As suggested by Robertson R. E., et al. [15], it is observed that the mechanism of the reaction change bimolecular to unimolecular [16] with increase in water concentration.

Table2: Change in logk values with log [H2O] at different range of temperature.

% of EG	% of H2O	Log [H2O]	3 + Log k				
			20°C	25°c	30°c	35°c	40°c
30%	70%	1.569	1.430	1.745	2.030	2.320	2.600
40%	60%	1.522	1.375	1.669	1.950	2.215	2.485
50%	50%	1.4437	1.329	1.600	1.860	2.105	2.360
60%	40%	1.346	1.250	1.520	1.769	2.000	2.245
70%	30%	1.221	1.200	1.420	1.630	1.830	2.030

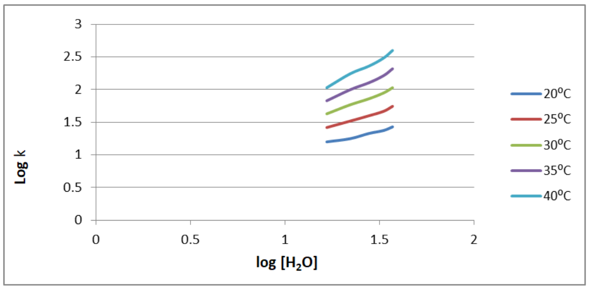

Figure1: Plot of log [H2O] with Log K

Table3: Calculated values Slopes of logk verses log [H2O] Water-acetone media

Temp°C	Slope
20°c	1.169
25°c	1.372
30°c	1.538
35°c	2.191
40°c	2.346

Activation Parameters of reaction (ΔH* ΔG* and ΔS*):

Activation parameter, like activation energy also plays an important role in ester hydrolysis. Wynne-jones and Eyring equation. [17] Are used to calculate all these parameters and the result are inserted in Table-4 with increasing mole% of solvent. The change in free energy of activation (ΔG*) with solvent composition is appear to be very small and considered to be negligible. This behaviour of (ΔG*) was also shown by [18, 19]. Again, decrease in entropy of activation with solvent composition attributed that the conversion of final state to transition state together with decrease in Entropy. It also inferred that transition state is more solvated as compared to initial state with increase of solvent composition.

Large change in (ΔH*) and (ΔS*) with negligible change in (ΔG*) with varying composition of solvent usually attributed enthalpy entropy compensation effect. [20]. such compensation effect generally result in linear relationship between (ΔH*) and (ΔS*). The plots of (ΔH*) verses (ΔS*) for the investigated ester, are also found linear (fig-5) and follows Barclay and Butler rule [21 22]. The slope of this line is called iso-kinetic temperature which comes to be 265. This suggested that very little interaction between the solvent and solute take place.

Table4: Thermodynamics Activation Parameters ($\Delta H^*$and ΔG^* in KJ/Mole, ΔS^*in J/K/Mole)

% of EG	Mole %	ΔH^* in KJ/Mole	200 C		250 C		300 C		350 C		400 C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
30%	9.56	99.72	90.80	30.44	90.55	30.77	90.49	30.46	90.27	30.68	90.11	30.70
40%	14.11	94.86	91.11	12.79	91.03	12.85	90.96	12.87	90.89	12.88	90.83	12.87
50%	19.77	90.18	91.37	-4.061	91.42	-4.16	91.48	-4.290	91.54	-4.41	91.55	-1.182
60%	26.99	85.41	91.73	-21.56	91.86	-21.64	92.01	-21.78	92.16	-22.20	92.25	-21.85
70%	36.52	77.91	92.10	-48.43	92.43	-48.72	92.82	-48..08	93.17	-49.54	93.54	-49.93

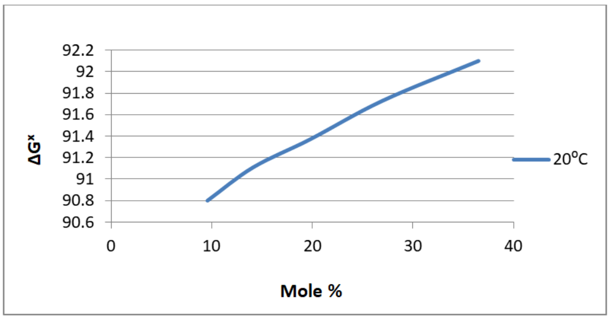

Figure2: plot of ΔG^* verses mole % at 200c

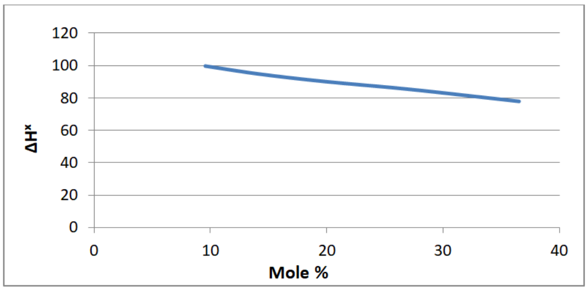

Figure3: plot of ΔH^* against mole %

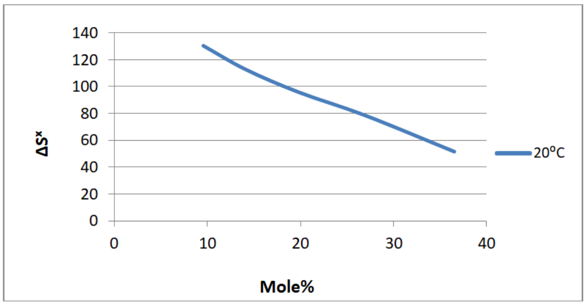

Figure4: plot of ΔS^*+100 versus mole %

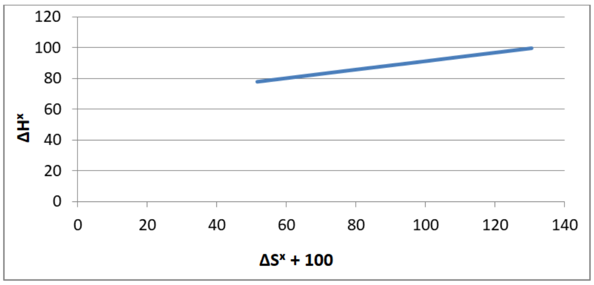

Figure5: plot of ΔH^* with ΔS^*+100 at 200C (water-Acetone) system

CONCLUSION

Result obtained shows that the values of rate decrease with successive addition of solvent which indicate that both salvation and dielectric change are responsible for decrease in rate.

The plots of Logk verses log [H2O] were found to be 1.16 to 2.34 with increasing temperature. This result shows that the nearly1.16 to 2.34 water molecule take part in formation of activated complex with increase of temperature. Small change in free energy of activation with large change in (ΔH^*) and (ΔS^*) appear to be enthalpy- entropy compensation effect. Linear plots of (ΔH^*) verses (ΔS^*) justified the iso- kinetic relationship.

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