

Kinetic study of solvent dynamics for the hydrolysis of Propyl Methanoate in an aqueous solvent system

Abstract

The rate of acid-catalyzed hydrolysis of propyl methanoate has been studied in different compositions (30 to 70%) of an aqueous mixture of propyl-2 (v/v) over a range of temperatures (20 to 40⁰ °C). The rate of reaction decreases with increasing proportion of solvent fraction. The Arrhenius plots have been employed to determine the iso-composition activation vigor and iso-dielectric activation vigor, which indicate the extent of solvent-solute interaction in the reaction media. Wynne Jones and Eyring's equation has been used to determine the thermodynamic parameters in terms of the salvation effect.

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Introduction

With a change of solvent composition in an aqueous solvent system, the rate of reaction is changed, which actually has actual great impact in the chemical industry as well as in the chemical laboratory. In this project, we have discussed the acid hydrolysis of propyl methanoate, which is used as a food additive and flavoring agent, and also as a djuvant. In this study, an attempt has been made to observe the effect of solvent in water, propanol-2, solvent system in the presence of acid. Several reports have been found earlier [1-5] for the hydrolysis of different esters, but there is no satisfactory report published on acid-catalyzed hydrolysis of methanote ester, particularly in an aqueous solvent system. The earlier report of Ingold [6] and Laidler [7] showed that with increasing dielectric constant, the rate of reaction increases. However, Parker [8] and Roberts [10] found the reverse order. That is rate of reaction decreases with an increase in dielectric constant.

Materials and Methods

The tapering flask contains the explanation, and a small Stoppard bottle containing pure propyl methanoate has been thermostated for 30 minutes. Calculated amount of organic solvent (propanol-2) and water, and stock acid (HCl) have been mixed in a 250 ml conical flask in such a way that the total volume of the solution was 50 mL and its strength became 0.5M. After that, 0.60 ml of ester has been withdrawn and added rapidly to the acidic solution of the water-solvent combination. Now, immediately, 2 mL of an aliquot of the reaction concoction was inhibited and allowed to run into a conical flask containing 25mL of ice-cold water so that the reaction may be

arrested quickly. The acid solution was titrated with standard baryitha solution using phenolphthalein indicator. The stop clock was started when half of the aliquot was added to ice-cold water. The time has been assumed as a starting time or zero time. Considering the zero time, the rest of the ester was estimated with a definite intermission of time.

Result and Discussion

3.1 Solvent Effect Dependence and Rate Constant

The specific rate constant of propyl methanote has been measured in a water-propanol-2 system. The rate constant is calculated with plots of $\log k$ against the reciprocal of time. The calculated values are tabulated in Table 1. The retardation of the rate with increasing proportion of organic solvent(Fig. 1) may be inferred that the polarised transition state is disfavoured with increasing proportion of solvent. The addition of an OH-ion to the carbon of the carbonyl group of the ester, followed by a quick reaction with water, is the step that dictates the pace of solvolysis. According to Tommila et al. [11], the reaction rate must thus drop if the hydroxyl ion's activity does. As the concentration of free water accessible for salvation rises, the interaction between water and propanol increases, as indicated by the lower rate in the water-propanol system.

The plots of $\log k$ against mole% represent the smooth decrease in rate[fig-2], which indicates that hydroxyl ion is tougher, hence the rate is decreasing. [12,13].

Table 1

Bimolecular rate constant $k \times 10^4(\text{dm})^3/\text{mole}/\text{mint}$

Temp in °C	% of propanol-2				
	30%	40%	50%	60%	70%
20°C	53.08	44.15	36.30	30.19	21.87
25°C	108.89	93.32	77.62	66.03	51.88
30°C	201.83	177.82	154.88	133.35	108.39
35°C	363.07	354.81	288.40	254.09	217.27
40°C	676.08	609.53	562.34	501.18	446.68

Table 2

log k values with different mole%

Percentage of propanol-2	Mole%	3+ log k				
		20°C	25°C	30°C	35°C	40°C
30	9.12	1.725	2.037	2.305	2.560	2.835
40	13.64	1.645	1.950	2.250	2.550	2.785
50	19.16	1.560	1.895	2.190	2.460	2.750
60	26.23	1.480	1.820	2.125	2.405	2.700
70	35.61	1.340	1.715	2.035	2.337	2.650

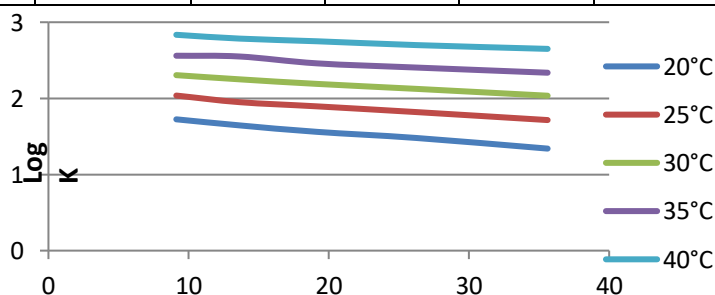


Fig. 1. Plots of $\log k$ with mole%

3.2 Activation Energy (E_c) & Rate of Reaction:

The values of activation energy (E_c) have been considered with the support of Arrhenius plots, and the obtained value has been inserted in Table 4. By the observation of Table 4, it has been found that activation energy increases from 93.46 to 114.16 KJ/mol.

The cause of enhancement in (E_c), in this binary solvent, is due to solvation in the early state and desolvation in the conversion state. [13,14]

Table 3

Temp in °C	$10^3/T$	3+ Logk				
		30%	40%	50%	60%	70%
20°C	3.412	1.725	1.645	1.560	1.480	1.340
25°C	3.355	2.037	1.950	1.895	1.820	1.715
30°C	3.300	2.305	2.250	2.190	2.125	2.035
35°C	3.247	2.560	2.550	2.460	2.405	2.337
40°C	3.195	2.830	2.785	2.750	2.700	2.650

Different log k values as a purpose of temperature

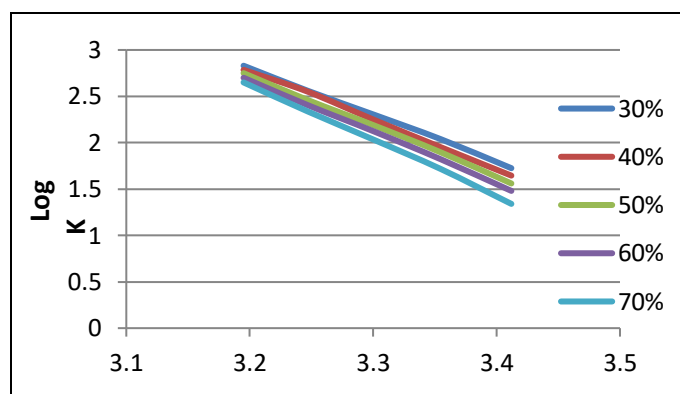


Fig 2. Plots of log k with $10^3/T$

Table 4

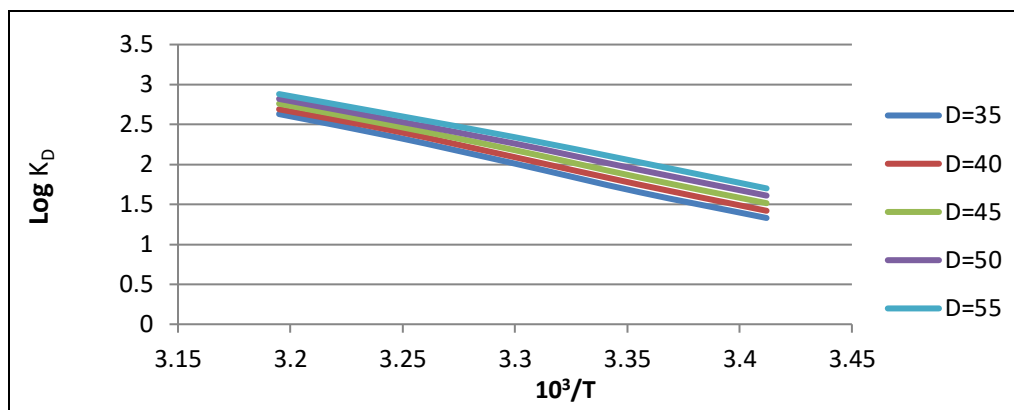
Iso- Composition activation energy at different solvent fractions

% of E_c	30%	40%	50%	60%	70%
E_{exp} in KJ/mole	93.46	99.01	103.60	104.83	114.16

Table 5

The values $\log k_{DAt}$ different D

Temp in °C	$10^3/T$	D=35	D=40	D=45	D=50	D=55
20°C	3.413	1.330	1.420	1.515	1.610	1.700
25°C	3.356	1.655	1.749	1.840	1.935	2.030
30°C	3.300	2.010	2.090	2.178	2.260	2.340
35°C	3.247	2.340	2.415	2.480	2.545	2.615
40°C	3.195	2.630	2.690	2.760	2.820	2.880


 Fig. 3. Difference of $\log k_d$ with $10^3/T$

3.3 Dielectric Effect on Reaction Rate:

The solvent outcome on reaction rate may similarly be the effect of the dielectric continual on reaction rate. A rate increase normally increases the rate. For the ion-dipole reaction, a linear plots are obtained by plotting the $\log k$ against D or $1/D$. With the slopes of the curve at constant D , the values of iso-dielectric composition energy were calculated and tabulated in Table 6. By the observation of the above table 6 and fig-3, it has been found that, decrease in iso-composition dielectric energy (E_D) values are similar to iso-composition activation energy, which was recently supported by different authors.[15]

Table 6

Intended values of (E_D) at constant D

Dielectric constant(D)	D=35	D=40	D=45	D=50	D=55
E_D in KJ/mole	118.70	116.79	115.00	111.27	93.83

CONCLUSION

By the observation and analysis of the above project, it has been found that the rate of reaction decreases gradually addition of solvent to the reaction media. Iso-composition vigor and iso-dielectric stimulation energy have been calculated with the help of Arrhenius plots, which explain the effect of solvent on reaction media.

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