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Solvent effect and kinetics on Solvolysis of propyl Formate in water-propanol solvent mixture

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Abstract
The hydrolysis of propyl formate in binary water+propanol-2 mixture was investigated volumetrically for kinetic studies. The rate of reaction decreases continuously with decreasing concentration of water at all varying temperatures ranging from 20 to 40^0C.The iso-composition activation energy (E_C) rises with increasing proportion of solvent. The kinetics of the reaction was also investigated in term of solvent composition, water concentration and dielectric constant. The thermodynamic activation parameters were also calculated.

Keywords: acid catalised hydrolysis Solvent effect, propyl formate, Hydrolysis, water-propanol mixture. Specific rate constant, Iso-composition and Iso- dielectric Activation energy. Activated complex, salvation and desolvation Initial and transition state

1. Introduction

The influence of solvent on the rate and chemical change of alkali catalyzed hydrolysis of ester has received attention over the time [1-6], but very little attention has been paid so far on the studies of solvent effect on rate, the mechanistic path ways, solvent- solute interaction and various thermodynamic activation parameters of acid catalyzed hydrolysis of aliphatic higher formats which have an important medicinal and industrial importance. It also has the utility of a flavoring agent in additive of food supplement.

2. Experiment

Purified propanol of Merck grade and propyl format of made in USSR were taken into use. The kinetics of acid catalysed hydrolysis of ester was studied volumetrically by adding 0.45 ml of ester through graduated syringe pipette in 50 ml of 0.5M HCl solution. The values of specific rate constant were evaluated using first order rate equation which have tabulated in Table-1. The evaluated values Iso-composition activation energy and Iso dielectric activation energy is calculated by Arrhenius plots and is depicted in Table-4and Table-5 respectively. The number of water molecules involved in formation of activated complex of the reaction were evaluated from the slopes of the plots of log k verses log [H_2O] values from Table-6 and numerical values of slopes are recorded in Table-7.

The value of thermodynamic activation parameters have been evaluated using Wynne Jones and Eyring {7} equation and synchronized in Table-8

3. Result and Discussion

3.1 Effect 0f solvent on Specific Rate

For showing the solvent effect, on specific rate constant of the reaction rate, the logarithmic values of k have been plotted against mole% of added organic co solvent (propanol-2) of reaction media as shown in fig-1, From this fig-1 it is clear that rate of hydrolysis decreases regularly with addition of propanol-2 in reaction media. For explaination, in the rate, the view of Hughes and Ingod [8], the prediction of Laidler and Landskroener [9] and singh *et al*. [10]. come to rescue. According to them, rate of reaction should decrease with the depletion of the dielectric constant of media. Here with the increasing proportion of propanol or decreasing percentage of water the dielectric constant value of the medium also decreases.

It may also be inferred that retardation in rate is mainly due to:

(i) Decreasing the polarity of the medium as changing from polar to less polar water propan-2-ol medium.
(ii) Lowering of the bulk dielectric constant values of the medium.

These two factors are quite in operation and the interpretation is quite in agreement with theory proposed by three groups of workers as noted above. The rate is bound to decrease with decreasing dielectric constant of the medium. Earlier Singh AK [11]. Has reported similar result.

Table 1: Specific rate constant k x10^3(dm)^3/mole/mint] values of acid catalysed Hydrolysis of propyl formate in water- propanol

Temp in ^OC	% of propanol-2				
	30%	40%	50%	60%	70%
20^OC	56.23	44.66	37.93	30.90	25.40
25^OC	102.010	89.12	74.96	65.31	54.32
30^OC	194.98	194.98	153.10	128.82	112.20
35^OC	354.81	331.13	294.44	257.03	226.46
40^OC	645.65	616.59	562.34	501.18	547.08

Table 2: Variation of 3 + Log k Value against mole %, Water-propanol solvent System.

Temp in ^OC		3 + Log k				
	Mole%	20^OC	25^OC	30^OC	35^OC	40^0C
30%	9.33	1.750	2.010	2.290	2.550	2.810
40%	13.79	1.650	1.950	2.225	2.520	2.790
50%	19.35	1.579	1.875	2.185	2.469	2.750
60%	26.47	1.490	1.815	2.110	2.410	2.700
70%	35.90	1.405	1.735	2.050	2.355	2.660

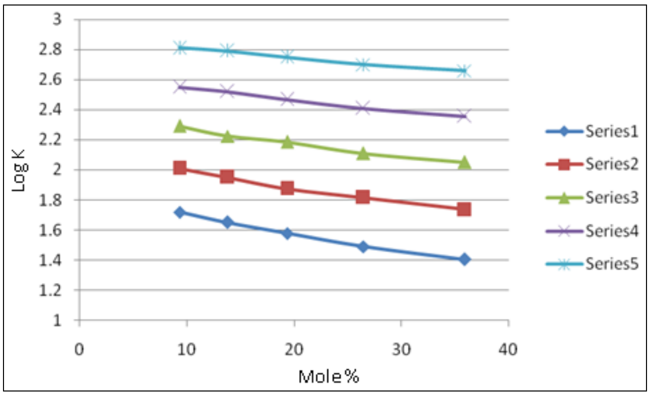

Fig 1: Variation of log k with mole %.

3.2 Solvent effect on Iso-composition Activation Energy of the reaction

On observing the data mentioned in table-4. We have observed that the value of iso- composition activation energy of the reaction goes on increasing from 94.81 to 112.00 KJ/Mole with increasing concentration of propanol from 30 to 70%(v/v),in reaction media.

The enhancement of iso-composition energy (E_C) energy values of reaction in water-propanol media may be due to any of the following three cases.

(i) Initial state is more solvated than the transition state
(ii) The initial state is less dissolved than transition state, and
(iii) The transition state is dissolved ted and initial state is solvated.

Among these three factors. The Third factor seems to be operative in this case and it has been supported by increase observed in the values of entropy of activation as mentioned in Table-8, this view has also recently been supported by Singh AK [12].

Table 3: 3+ Logk Value against 10^3/T, Water- propanol solvent system.

Temp in ^{O}C		3 + Logk				
	10^3/T	30%	40%	50%	60%	70%
20^{O}C	3.412	1.750	1.650	1.579	1.490	1.405
25^{O}C	3.355	2.010	1.950	1.875	1.815	1.735
30^{O}C	3.300	2.290	2.225	2.185	2.110	2.050
35^{O}C	3.247	2.550	2.520	2.469	2.410	2.355
40^{0}C	3.195	2.810	2.790	2.750	2.700	2.660

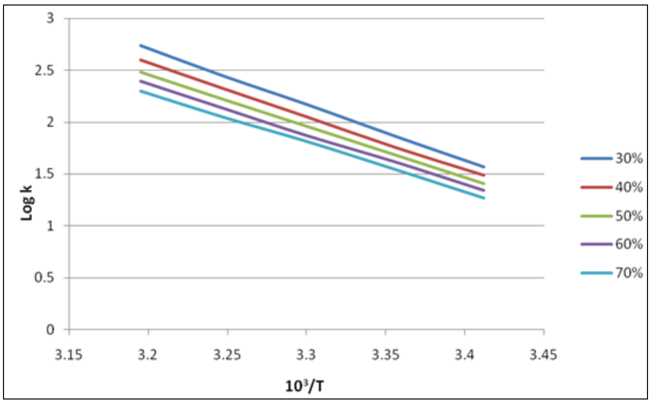

Fig 3: Variation of Log K with 10^3/T. (water-propanol media)

Table 4: Values of Iso-composition Activation Energy (water-propanol media)

% of Propanol	30%	40%	50%	60%	70%
E_{exp} in KJ/mole	94.81	100.49	104.82	106.62	112.00

3.2 Solvent effect and Iso- Dielectric Activation Energy.

With a view to minimise the dielectric effect, the iso-dielectric activation energy was evaluated from the slopes of the Arrhenius plots of log k_D values (obtained from interpolation of plots of log k value against D value of reaction media) against1/T and the value thus obtained have been tabulated in Table-5. From this table it is found that the E_D values goes on decreasing from 116.06 to 102.08KJ/M. with increasing D value from D=25 to D=45. This trend of depletion in E_D is in harmony with the enhancement in iso-composition activation energy (E_C) values with increasing concentration of propanol in reaction media. Such finding are quite natural and are supported recently by Singh RT *et al.* [13].

Table 5: Values of Iso-Dielectric Activation Energy (water-methanol)

Dielectric constant(D)	D=25	D=30	D=35	D=40	D=45
E_{exp} in KJ/mole	116.06	114.40	111.54	108.81	102.08

3.4 Effect of solvent on solvation number and on mechanistic pathways of reaction.

The solvation number i.e. the number of water molecules involved in the formation of activated complex of the reaction were evaluated from the slopes of log k values against log [H_2O] values of the reaction media using Robertson [14]. equation which is as follow-

$$\log k = \log k0 + n \log [H_2O]$$

Where n is the solvation number

The log k and log [H_2O] are enlisted in Table-6 and their plots are shown in fig-3. The numerical value of slopes of the plots has been recorded in Table-7. Robertson *et al.* [15]. have established that numerical value of solvation number (n) of water molecules associated with activated complex in its formation are fairly high for reaction with unimolecular mechanistic pathways and low for reaction following bimolecular mechanistic pathways. From the Table-7, it can be concluded that the number of water molecules associated with the activated complex of the reaction in the formation, decreases from 3.318 to 2.06 with increase in temperature from 20 to 40C. Thus, on guideline of Robertson *et al.* it may be inferred that with rise in temperature of the reaction, the mechanistic pathways of the reaction is changed from unimolecular to bimolecular in presence of propanol-2 in reaction media.

About the change in the structure of water in presence of propanol-2 and with rise in temperature of the reaction, water component of reaction media changes its structure from its bulky form to dense form at equilibrium.

$$[H_2O]_b \longleftrightarrow [H_2O]_d$$

This finding and such interpretation has also been supported by Singh AK [16].

Table 6: Variation of Log [H_2O] against Log k (water-propanol media)

% of Acetone	% of H_2O	Log [H_2O]	3 + Log k				
			20^0C	25^0c	30^0c	35^0c	40^0c
30%	70%	1.5690	1.750	2.010	2.290	2.550	2.810
40%	60%	1.5229	1.650	1.950	2.225	2.520	2.790
50%	50%	1.4437	1.579	1.875	2.185	2.469	2.750
60%	40%	1.3468	1.490	1.815	2.110	2.410	2.700
70%	30%	1.2218	1.405	1.735	2.050	2.355	2.660

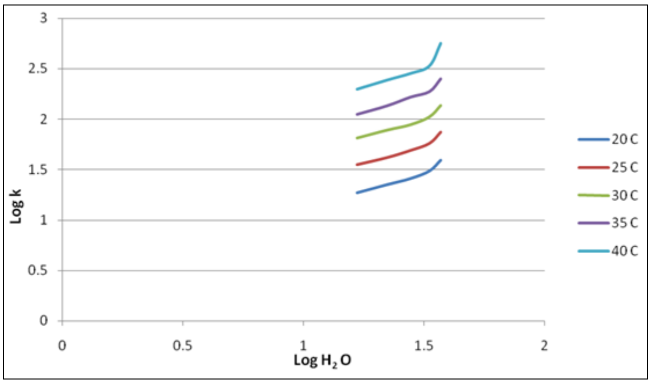

Fig 4: Variation of log [H_2O] with Log K. (water-propanol media)

Table 7: Calculated values of slopes (Plot of log k verses log [H_2O]) of Water-propanol-2 media

Temp^{0}C	20^0c	25^0c	30^0c	35^0c	40^0c
Slope	3.318	2.794	2.372	2.107	2.006

Table 8: Consolidated values of Thermodynamics Activation Parameters ($\Delta H^*$and ΔG^* in KJ/Mole, ΔS^*in J/K/Mole) of the reaction in Water-propanol Media.

% of propanol	Mole %	ΔH^* in Kj/Mole	20^0C		25^0C		30^0C		35^0C		40^0C	
			ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
30%	9.33	38.47	88.01	169.07	89.06	169.76	88.98	166.69	88.85	163.57	88.85	160.95
40%	13.79	40.75	89.53	166.48	89.40	163.69	89.36	160.42	89.08	156.91	88.97	154.05
50%	19.35	42.98	89.93	160.23	89.80	157.11	89.59	153.82	89.39	150.68	89.21	147.69
60%	26.47	44.13	90.43	158.02	90.63	156.04	90.03	151.48	90.06	149.12	89.75	145.75
70%	35.90	44.67	90.91	157.87	91.03	155.16	90.38	150.85	90.39	148.44	90.07	145.04

4. Conclusion

From this analysis of scheme, it is concluded that

1. The rate is bound to decrease with decreasing dielectric constant of the medium.
2. Enhancement in values of iso-composition energy inferred that the transition state is desolvated and initial state is solvated
3. The trend of depletion in E_D is in harmony with the enhancement in iso-composition activation energy (E_C) values with increasing concentration of propanol in reaction media.
4. Decrease in values of water molecules associated with activated complex inferred that, mechanistic pathways change from unimolecular to bimolecular with rise in temperature.

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