Solvent Effect and Mechanism of Solvolysis of Benzyl Formate in Water-Ethanol Media

Abstract

The study of the kinetics of the solvent effect on the mechanism of acid catalysed hydrolysis of Benzyl formate has been carried out in water Et-OH media having varying concentration of Et-OH from 30% to 80% at temperatures ranging from 293K to 313K at interval of 5K. Effect of change of concentration of the organic co-solvent of the reaction media (Water Et-OH) was minutely observed and quantitatively reflected in terms of number of water molecules associated with the transition state of the reaction. On the basis of the number of water molecule associated with the activated complex of the reaction, it was inferred that acid catalysed hydrolysis of Benzyl formate ester follows A_{AC}^2 mechanism. It behaves Enthalpy dominating in which path of reaction changed from unimolecular to bimolecular. It is concluded that in this reaction media (Water-Ethanol), there is appreciably strong solvent - solute interaction.

Keywords: Aromatic formate, Activation Parameters, Solvolysis, Mechanistic Path, Solvent-Solute interaction, specific rate constant, Dipolar, A_{AC}^2 mechanism.

Introduction

The Kinetic study of solvent effect on the rate and mechanism of the reaction has aroused much interest and enquiries in the mind of researchers. Various researchers[1-4] have reported about the solvent effect on the solvolysis of simple esters. But effect of water Et-OH solvent on the mechanism of acid catalysed solvolysis of Benzyl formate has not been paid even a little attention so far.Hence it has been proposed to study the solvent effect of ethyl alcohol on the mechanistic pathways of acid catalysed hydrolysis of Benzyl formate in water Et-OH media. So in order to highlight the above noted idea, it was thought essential to investigate about the fact that how the mechanism, thermodynamic activation parameters including activation energy and iso-kinetic temperature of acid catalysed hydrolysis of benzyl formate have been affected in Water-Ethanol reaction media having varying concentration of Ethanol. It was thought essential also because the study of such reactions seems very important and much useful from the medicinal as well as biological points of views.

Materials and Methods

The Kinetics of the acidic hydrolysis of Benzyl formate in water Et-OH media having varying concentrations of Et-OH from 30% to 80% (v/v) was studied at different temperatures ranging from 293 K to 313 K. Purified ethyl alcohol of BDH grade and Benzyl formate of USSR make was used. Before use of them was purified by the methods outlined by vogel. Glass apparatuses were also of corning brand. The Kinetics of acid catalysed hydrolysis of the ester was studied as usual by adding 0.4 ml of the ester in 50 ml of 0.5 M Hcl solution. The specific rate constant values, iso composition activation energy E_C, iso-dielectric activation energy E_D and no. of water molecule associated with the activated complex data of logK and 1/T have been evaluated and noted in table I, II, III, IV and V respectively.

Discussion on the Results

From Table-I, it is obvious that the rate of the reaction goes on decreasing with increasing mole % of the organic co-solvent in the media. It is clear that there is fast followed by slow depletion in the rate of reaction. The following two factors seem to be responsible for depletion in the rate of reaction in solution are (I) Lowering of the bulk dielectric constant values of

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the medium and (II) Decreasing polarity of the medium as changing from polar water to less polar water Et-OH medium. Our these explanations have also been supported by Laidler and Landskroener[5] and Hughes and Ingold[6] and recently by Srivastva and Singh[7].

Solvent Effect on Iso-composition activation Energy

The acid catalysed hydrolysis of Benzyl formate was found to obey Arhenious law as different range of temperatures. This law was verified by plots of logK against $\frac{1}{T}$ which is shown in figure 01. The data of logK and 1/T have been tabulated in table-V. From table II it is clear that values of iso-composition activation energy go on increasing from 87.95kJ/mole to 125.96 kJ/mole with addition of 30% to 80% ethyl alcohol in the reaction media. Enhancement in the values of iso-composition activation energy may be due to either of the following cases (I) When the transition state is desolvated more than the initial state (II) When the initial state is solvated more than the transition state and (III) When the initial state is solvated and the transition state is desolvated.

Solvent Effect on Iso-dielectric Activation Energy E_D

Log K_D values obtained from interpolation of the plots of log K values against D values. The values of iso-dielectric activation Energy (E_D) have been evaluated and are recorded in table-III. From this table it is inferred that E_D values goes on decreasing from 137.98 kJ/mole to 93.32 kJ/mole with increasing D values of the reaction media from 30 to 60. This trend of change in E_D values with increasing D values of the reaction media has also been supported by Wolford[8] and Rai and Singh et al[9].

Solvent effect and Iso-kinetic relationship

Barclay and Butler have developed iso kinetic relationship between enthalpy of activation ΔH^* and entropy of activation ΔS^* as follows.

$\delta m (\Delta H^*) = \beta \delta m (\Delta S^*)$ Where β is a constant called iso-kinetic temperature. The value of iso-kinetic temperature of the acid catalysed hydrolysis of Benzyl formate in water Et-OH media has been evaluated which comes to be 324. From the values of slope as table-IV, it is clear that when water concentration is below 41.2% in water Et-OH media, its values decreases from 0.974 to 0.348 with increasing temperature from 293K to 313K. Similarly the values of slope, when water concentration is above 41.2% the values of slopes decreases from 1.468 to 0.349 with rise in temperature from 293K to 313K.

Research Objective

A lot of work has been done on the acid catalysed hydrolysis of various ester in water and some other aquo-organic solvent mixtures and is proved that mechanism is bimolecular acyl fission. By the method of Sarkar and Rakshit[10] it can be concluded that A_{AC}^2 mechanism in aquo Et-OH system. The acidic hydrolysis of Benzyl formate ester as it is fruitful from food technological as well as medicinal points of views. During the research on the topic evaluate the value of specific rate constant, activation energy, iso- kinetic temperatures and no. of water molecules.

Conclusion

It can be concluded that with rise in temperature the number of water molecules associated with the activated complex increases as the proportion of the organic co-solvent decreases in water Et-OH mixture and it explains that the dense form of the water is changed to its bulky form when alcohol is added to water. Which is observed by Packer and Tomllinson[11].
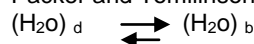
$(H_2O)_d \rightleftharpoons (H_2O)_b$

Table-1
Specific rate constant values for acid catalysed hydrolysis of Benzyl formate in Water Et-OH media
$K \times 10^2$ in Min^{-1}

Temp. in K	% of Ethyl Alcohol in Water Et-OH Media					
	30%	40%	50%	60%	70%	80%
293 K	71.32	57.16	44.18	35.16	25.65	18.64
298 K	150.73	110.94	89.37	74.20	57.82	44.36
303 K	244.12	211.93	182.47	157.43	128.85	103.80
308 K	436.72	390.93	354.73	315.06	272.96	231.26
313 K	790.86	718.79	684.07	631.68	576.77	510.63

Table II
Value of Iso-composition Activation Energy of the reaction in water-EtOH media.

%of Ethyl Alcohol	30%	40%	50%	60%	70%	80%
E_c in KJ/mole	87.95	96.59	104.28	109.64	119.20	125.95

Table III
Iso-Dielectric Activation Energy values of the reaction at different dielectric constant values of water-EtOH media:

Dielectric Constant	D=30	D=35	D=40	D=45	D=50	D=55	D=60
E_D values in KJ/mole	137.89	133.17	122.58	112.80	106.91	101.14	93.32

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Table-IV

Values of the slopes of the plots of log K versus log [H₂o] at different temperatures:

Temp in K	Slope-I Below log [H_2O] = 1.36	Slope-II Above log [H_2O] =1.36
293 K	0.974	1.468
298 K	0.745	1.442
303 K	0.616	0.944
308 K	0.433	0.615
313 K	0.348	0.348

Table V

Variation of $\log \frac{k}{T}$ values with $\frac{10^3}{T}$ values in water- EtOH media:

Temp in K	$\frac{10^3}{T}$	$3+\log \frac{K}{T}$ values					
		30%	40%	50%	60%	70%	80%
293 K	3.413	1.3863	1.2902	1.1783	1.0791	0.9422	0.8035
298 K	3.356	1.7039	1.5708	1.4770	1.3962	1.2878	1.1727
303 K	3.300	1.9061	1.8447	1.7797	1.7156	1.6286	1.5347
308 K	3.249	2.1516	2.1035	2.0613	2.0098	1.9475	1.8755
313 K	3.195	2.4025	2.3610	2.3395	2.3049	2.2654	2.2125

Fig. 01
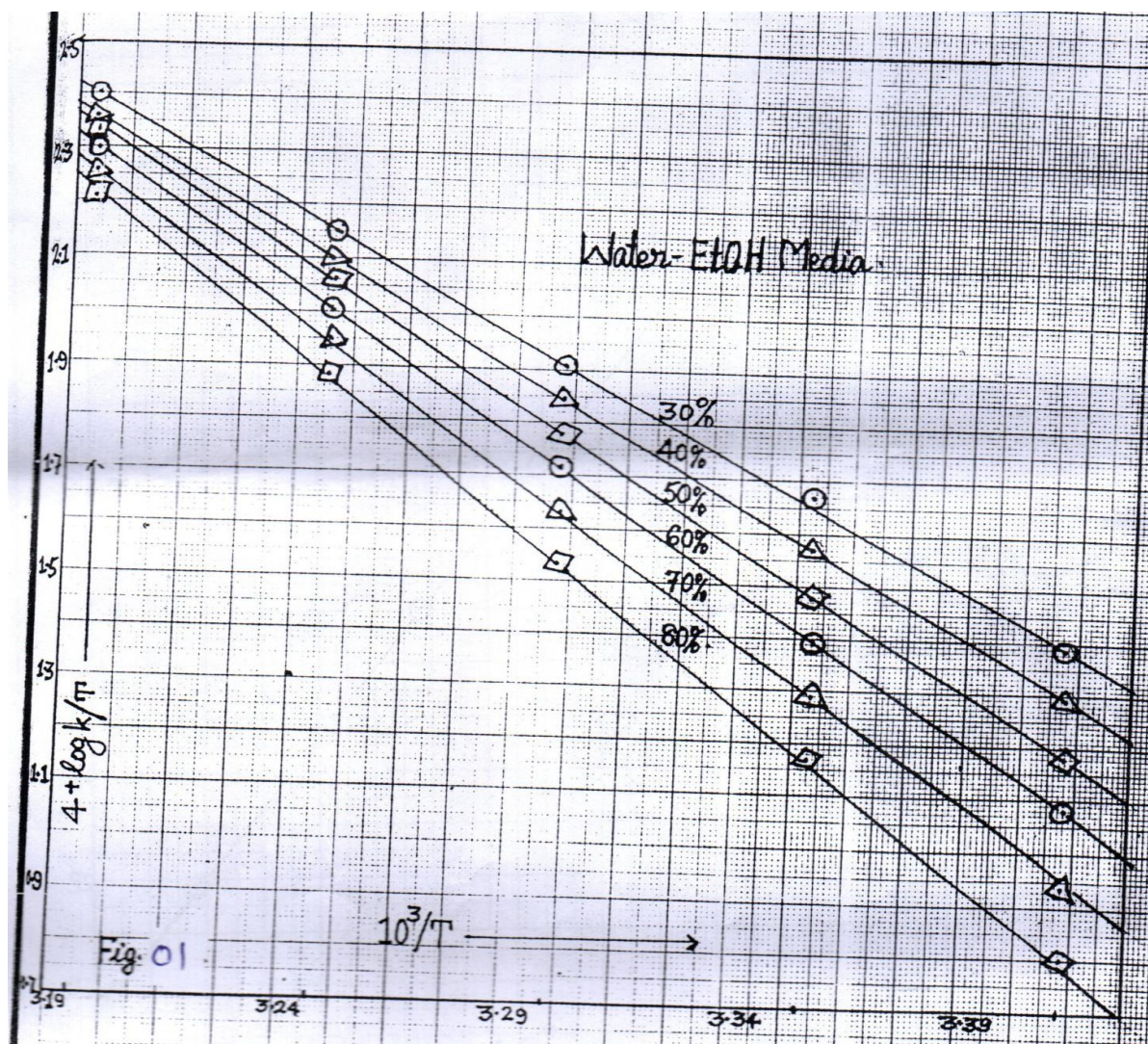
End Notes

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