

A Kinetic Study of the Solvent effect on the Solvolysis of Benzyl Methanoate Ester in water E_G media



Rameshwar Dubey

Senior Lecturer,
Deptt. of Chemistry,
R.B.D. Inter College,
Thepahan, Siwan, Bihar, India

P.R. Pandey

Retired University Professor,
Deptt. of Chemistry,
D.A.V. P.G. College,
Siwan, Bihar, India
(J.P. University, Chapra)

Abstract

The acidic hydrolysis of Benzyl methanoate ester was carried out in water- E_G (Ethylene Glycol) media in which the composition of the organic co-solvent was varying concentration from 30% to 80% (v/v) at temperatures ranging from 293K to 313K. Explanations for the decrease in the values of specific rate constants, decrease in E_D values, effect of [H⁺] on the rates of hydrolysis have been given at appropriate places below. This gives idea about acidic hydrolysis of Benzyl methanoate ester with help of rate constant K and Iso-dielectric activation Energy (E_D). The initial sharp decrease followed by slow but smooth depletion in the rate with gradual addition of the organic co- solvent in the reaction media and with increasing temperature of the reaction has been explained in the light of solvation or desolvation of initial and transition state to the different extent. The changes in the values of Iso-dielectric activation energies of the reaction have been evaluated. Effect of ionic strength and [H⁺] ion reveals that the reaction is of ion-dipole type and it follows A_{AC}² mechanism.

Keywords: Iso-dielectric activation energy (E_D), specific rate constant, ionic strength, A_{AC}² mechanism, Activation Parameters, Dipolar, Ethylene Glycol (E_G), Aromatic Formate, Solvolysis, Mechanistic Path, Solvent-Solute interaction.

Introduction

Solvent plays a very important role in modifying the rate of reaction. A lot of work have been done on the solvent effect by various workers in several aqua-organic co-solvent systems but the effects exerted by dipolar solvent, EG have not been studied in detail, particularly at low and high concentrations of the solvent. In the present case, the dipolar solvent EG has been selected for studying the solvent effect on the hydrolysis of benzyl methanoate catalysed by an acid. So in order to highlight the above noted idea, it has been proposed to make a kinetic study Iso-dielectric activation energy (E_D) in acidic hydrolysis of benzyl methanoate ester in water-Ethylene Glycol (E_G) media.

Materials and Methods

Though the hydrolysis reactions of various types of ester have been carried out by various workers in several aquo-organic co-solvent systems. Purified ethylene glycol of BDH grade and Benzyl methanoate of USSR were made into use. The kinetics of acid catalysed hydrolysis of the ester was studied as *usual*^{1,2} by adding 1 ml of ester in 100 ml of 0.02M Hcl solution. Before use each of them was purified by the methods outlined by Vogel. Glass apparatuses were also of Corning brand. The solutions were used with appropriate precautions. The specific rate constant values, activation parameter, viz., Iso-dielectric activation energy (E_D) and effect of [H⁺] on the rates of hydrolysis and values of logK_D at fixed D values of water-E_G media have been given in table I, II, III and IV respectively.

Discussion

Effect of organic Co-solvent (E_G) on the rates

Table-I shows that the rate constant values of the reaction decrease with successive additions of EG in the reaction media at all temperatures. The rate retarding factors are (I) lowering of the bulk dielectric constant values of the medium and (II) decrease in the polarity of the medium with change from polar water to less polar water - EG medium. This is quite in agreement with the theory of *Day and Ingold*^{3,4} which states that the rate is bound to decrease with decrease in dielectric constant of the medium. This observation is also supported by *Laidler and*

*Landskroener*⁵. Similar effect produced by EG has also found support from *Singh et al*⁶.

Effect of solvent on the Iso-dielectric activation Energy (E_D)

The evaluation of Iso-dielectric activation energy (E_D) was thought essential for water-EG medium. From the values of slopes of the plots of log K_D values (obtained as interpolated values from the plots of log k values of the reaction against 'D' values of water-EG media) against $\frac{1}{T}$, the values of Iso-dielectric activation energy, E_D of the reaction have been calculated and are enlisted in Table II. From the table it is clear that with increase of dielectric constant of the medium, E_D values are increasing. On increasing the value of D from 46 to 70, the values of E_D are found to increase from 65.36 to 115.75 kJ mol⁻¹ respectively. By increase in the values of E_D corresponding to increase in the values of D, we mean that as more and more EG is added to water-EG solvent system, the dielectric constant of the medium decreases and subsequently there is decrease in the E_D values of the reaction. In other words, with the addition of EG to water-EG mixture, the E_D values of the reaction occurring in the medium are decreasing.

The trend of decrease in E_D values for acid hydrolysis of Benzyl methanoate with increasing EG content in water-EG medium is quite in agreement with the observation of *Wolford*⁷ as observed in case of water-EG solvent system.

Effect of $[H^+]$ ion on the rates of hydrolysis of Benzyl methanoate ester in water - E_G media

Acid catalysed hydrolysis of Benzyl methanoate in water- E_G media depends upon the concentration of $[H^+]$. The effect of change in acid concentration on the hydrolysis of Benzyl methanoate was studied at a fixed ionic strength ($\mu=0.9$) by adding requisite quantities of KCl and also at fixed solvent

composition of the medium (30%). The calculated values of specific rate constant corresponding to different strength of acidic solution as well as variation of log k values with log $[H^+]$ have been given in Table III. The plots of log k values versus log $[H^+]$ yielded a good straight line having a slope of 1.019. The value of this slope which is nearly equal to unity clearly indicates that acid hydrolysis of Benzyl methanoate in water-EG media follows A_{AC}^2 mechanism as recorded by *Zucker & Hammett*⁸. The plots of log k_D against D of water-EG media are good straight line are also in agreement with the *Elsemongy's*⁹ equation.

$k = k' e^{\alpha(D-1)}$ where k is the specific rate constant and k' is its value at $D=1$ and α is a constant. The values of log k_D were plotted against $\frac{1}{T}$ from their values as recorded in Table-IV and the slopes of the straight line as shown by figure-01.

Objective of the Study

A large number of researchers working in the field of chemical kinetics but study of the solvent effect of organic co-solvent E_G of solvolysis reaction of the aromatic methanoate ester has not been paid the attention. It is very important from medicinal as well as biochemical points of views.

Conclusion

The value of Iso-Kinetic temperature of the acid catalysed hydrolysis of Benzyl methanoate in water E_G media has been evaluated which comes to be 265 which is much less than 300.

It is concluded that there is a slow change in the structure of reactants or in the solvent or in both due to weak interaction between solvent and solute present in the reaction media consisting of E_G in the similar way as reported by *Leffler*¹⁰, our this conclusion has also been recently supported by *kumari and Singh*¹¹.

Table- I
Values of specific rate constant for Acid catalysed hydrolysis of Benzyl methanoate in Water-EG media
 $k \times 10^2$ in min⁻¹

Temp in K	% of EG (v/v)					
	30%	40%	50%	60%	70%	80%
293	58.69	52.24	46.14	41.11	36.99	31.20
298	110.94	95.26	79.52	68.74	57.03	44.58
303	211.40	173.72	138.04	113.50	87.26	63.10
308	382.03	302.69	231.26	181.18	130.92	88.53
313	691.51	532.23	388.24	288.93	194.94	122.49

Table- II
Values of Iso-dielectric Activation Energy (E_D) of the reaction at fixed 'D' values of water- EG media

D values	D=46	D=50	D=54	D=58	D=62	D=66	D=70
ED values in kJmol ⁻¹	65.36	72.09	78.62	89.58	93.94	102.11	115.75

Table- III
Dependance of Rate constant on $[H^+]$ at constant m for Acid Catalysed Hydrolysis of Benzyl methanoate in water- EG media

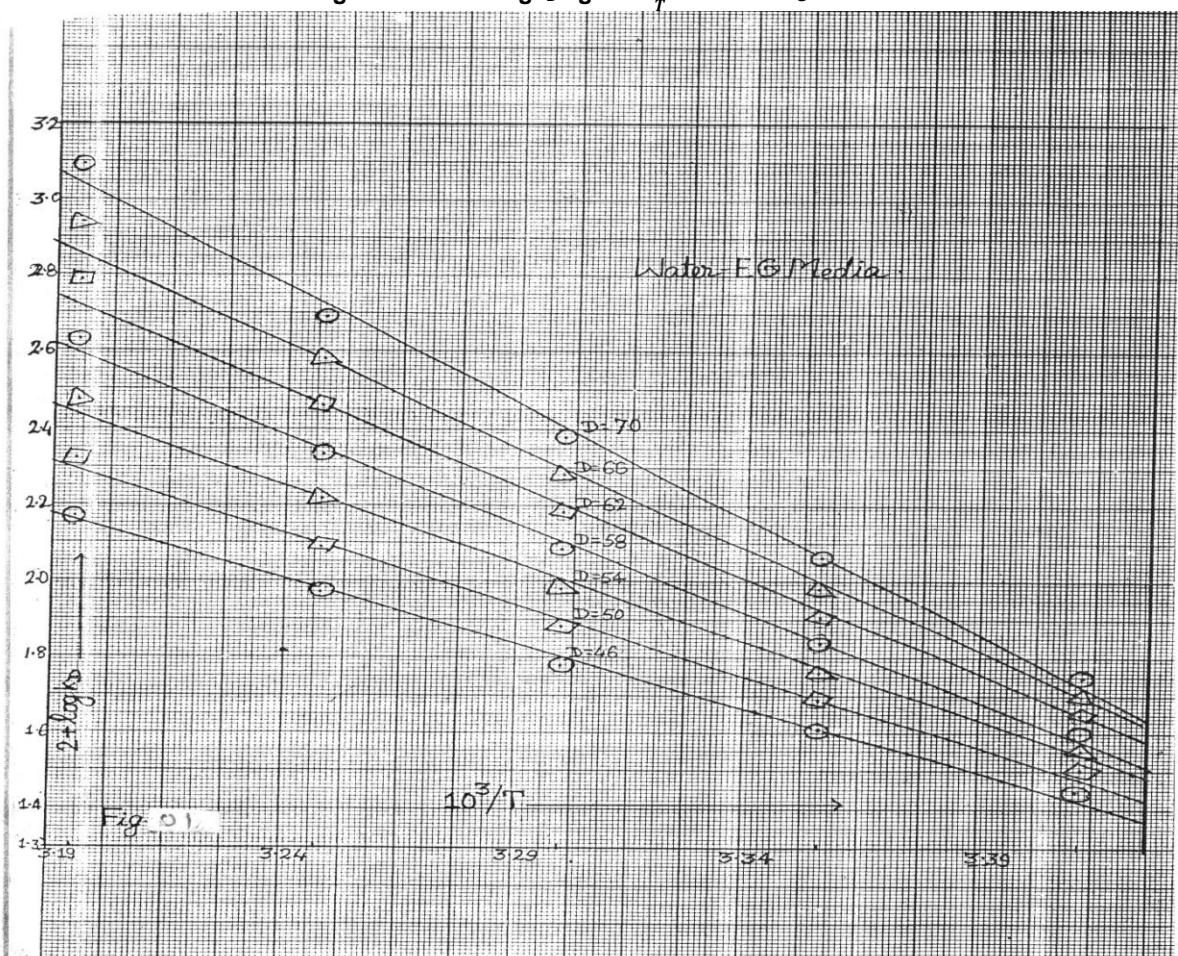
EG= 30% (v/v)		Temperature- 303 K				
$[H^+]$	[KCl]	μ	$k \times 10^2$ in min ⁻¹	2+log $[H^+]$	2+log k	Slope
0.10	0.80	0.90	42.19	1.000	1.6252	
0.15	0.75	0.90	63.10	1.1761	1.8000	
0.20	0.70	0.90	84.33	1.3010	1.9260	
0.25	0.65	0.90	106.62	1.3979	2.0261	
0.30	0.60	0.90	126.85	1.4771	2.1033	

0.40	0.50	0.90	169.43	1.6021	2.2290	1.019
0.50	0.40	0.90	211.40	1.6990	2.3251	
0.60	0.30	0.90	255.56	1.7782	2.4075	
0.70	0.20	0.90	300.68	1.8451	2.4781	
0.80	0.10	0.90	340.41	1.9031	2.5320	

Table- IV

Interpolated values of $\log k_D$ at fixed D values of the water-EG media

Temp. in k	$\frac{10^3}{T}$	D=46	D=50	D=54	D=58	D=62	D=66	D=70
293 k	3.413	1.446	1.498	1.548	1.598	1.648	1.698	1.749
298 k	3.356	1.612	1.687	1.761	1.835	1.907	1.983	2.058
303 k	3.300	1.781	1.881	1.980	2.082	2.181	2.280	2.380
308 k	3.247	1.968	2.091	2.215	2.335	2.456	2.577	2.692
313 k	3.195	2.167	2.321	2.475	2.628	2.785	2.937	3.095

Fig - 01 Plots of $\log k_D$ against $\frac{1}{T}$ of water -EG media

End Notes

1. Singh Lallan, Singh R.T. and Jha R.C.: J.Indian Chem. Soc; 58, 966, 1981
2. Singh, A; Singh, Atulit, Sinha, S. and Singh, R.T.: NIRJ Sci; 2, 69-74, 2009
3. J.N.E. Day & C.K. Ingold: Trans. Faraday Soc., 1941, 37, 686.
4. C.K. Ingold: "Structure and Mechanism in Organic Chemistry", 2nd edition, Cornel University Press, Ithaka, New York, 1967.
5. K.J. Laidler & P.A. Landskroener: Trans. Faraday Soc., 1956, 52, 200
6. P.Singh, R.I. Singh, P.K. Singh, A.B. Pandey & R.T. Singh: A.R.J. Phys. Sci., 2006, 9, No. (1-2), 135-137.
7. R.K. Wolford: J.Phys. Chem., 1964,68,3392.
8. L.Zucker and L.P. Hammett: J. Am. Chem. Soc., 1939, 61, 2791.
9. M.M. Elsemongy : Z.Physik chem. (neue Folge) 1973,84,294
10. Leffler J.E. : J.org. Chem; 20, 1201, 1955
11. Kumari Vibha, Kumari Sobha, Kumari, K. and Singh, R.T.: NIRJ Sci; 3 ,87-91,2009