

Solvent Effect on the Enthalpy and Entropy of Activation for the Hydrolysis of Ethyl Cinnamate in Mixed Solvent System

Singh AK*

Department of Chemistry, Teerthanker Mahaveer University, Moradabad, India

Abstract

The rate of alkaline hydrolysis of ethyl cinnamate was measured over the temperature range of 20°C to 40°C in water-acetone mixture at different composition 30 to 70% (v/v). The influence of solvent variation on reaction rate was examined in term of changes in the Activation parameter. Depletion of ΔH^\ddagger and ΔS^\ddagger value with simultaneous increase in ΔG^\ddagger of the reaction in reaction media, reveals that the reaction is Enthalpy domination and Entropy controlled. The Iso- dielectric activation energy (E_D) of reaction was found to decrease from 52.43 to 47.28. The Values of Iso-kinetic Temperature which is less than 300, clearly indicates that there is no appreciable interaction between solvent and solute present in the reaction media, i.e., reaction is not ion-dipole but ion-molecule type.

Keywords: Activation parameter; Solvent-solute interaction; Iso-kinetic temperature; Specific solvation; Iso dielectric activation energy

Introduction

Solvent play an important role in determining chemical reactivity. In particular, the rate of an elementary chemical reaction may change by orders of magnitude when solvent is changed. Kinetic solvent effect on chemical reaction in different media is correlated in terms of "solvent polarity" which is sums of all the specific and non-specific interaction of the media with initial and transition state". A large effort has been directed towards understanding such solvent effect and a great deal of progress has been made recently [1-3] both theoretically and experimentally. However, the interpretation of kinetic result on the solvent polarity on medium some time fails and sometime succeeds. In this note, we have extended our studies on kinetic solvent on well-known base catalyzed hydrolysis of Ethyl cinnamate, which is important for use of adding to cigarettes and cut tobacco, that are used for flavor agent and fragrance agent.

Experimental

The kinetics of base catalyzed hydrolysis of ethyl cinnamate has been carried out in water-acetone and having different concentration of solvent (acetone), varying from 30 to 70% (v/v) at five different temperature ranging from 20°C to 40°C at regular interval of 5°C. The specific rate constant calculated using second order reaction was found decrease with increase of acetone content, tabulated in Table 1 The iso dielectric Activation energy (E_D) is also calculated with help of slope of $\log k_p$ against $10^3/T$ at constant and tabulated in Table 2. The iso kinetic temperature was calculated with help of Barclay and Butler relation. The evaluated thermodynamic activation parameter has been tabulated in Table 3.

Result and Discussion

Solvent effect on rate of reaction

In order to discuss the variation of specific rate constant values with gradual addition of dipolar aprotic organic solvent (acetone) in reaction media, the value $\log k$ tabulated in Table 1. The decrease observed in specific rate constant (Table 1), with increasing concentration of organic solvent is probably due to depletion of Dielectric constant of media and solvation change taking place in media [4].

Solvent effect and thermodynamic activation parameters

The thermodynamics Activation parameter such as Enthalpy of Activation (ΔH^\ddagger), Entropy of Activation (ΔS^\ddagger) and free energy of Activation (ΔG^\ddagger), are better indicator of the solvent effect exerted by the solvent on the solvolysis reaction. These thermodynamics Activation parameter has been calculated with help of Wyne-Jones Eyring [5] equation and absolute rate theory [6] and placed in Table 4.

On careful observation of the data Tabulated in Table 4 (water-acetone) ΔG^\ddagger value in case of water-acetone increases from 92.09 to 94.26 KJ/mole with change of proportion of solvents from 20% to 70% at 20°C. Though the enhancement is not large, however it is quite considerable (Figure 1). The report of Yagil et al. [7] indicate that OH^- ion of NaOH is hydrated with three molecules of water. In mixed aquo-organic co-solvent mixture, the organic component molecules are expected to contribute to the process of desolvation as they may be regarded as poor anion solvater in comparison to water. A similar variation in ΔG^\ddagger values with increasing mole % of organic co solvent has been reported by Tommila [8] and Cleave [9] and recently Singh [10]. The variation of ΔG^\ddagger with mole % in the solvent are non-linear and increase smoothly with gradual addition of the solvent (Figure 2).

This finding is indicative of solvation or desolvation of reactant as explained by Absolute Reaction rate theory and supported by Elsemongy [11] and Singh [12]. From data mention in the Table 3, the interesting feature comes in the light is that out of all the value of three thermodynamic parameters ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger , the value of ΔH^\ddagger and ΔS^\ddagger goes on decreasing with simultaneous increase in G^\ddagger values with increasing proportion of acetone at all the temperature of the reaction, i.e., from 20°C to 40°C. From the fundamental thermodynamic equation

*Corresponding author: Singh AK, Department of chemistry, Teerthanker Mahaveer University, Moradabad, India, Tel: 05912360500; E-mail: anilkumar2_singh@yahoo.com

Received March 04, 2017; Accepted March 13, 2017; Published March 20, 2017

Citation: Singh AK (2017) Solvent Effect on the Enthalpy and Entropy of Activation for the Hydrolysis of Ethyl Cinnamate in Mixed Solvent System. J Phys Chem Biophys 7: 238. doi: 10.4172/2161-0398.1000238

Copyright: © 2017 Singh AK. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Temp in °C	% of ACETONE				
	30%	40%	50%	60%	70%
20°C	15.66	11.22	10.00	8.12	6.45
25°C	20.89	16.59	13.48	10.59	8.49
30°C	27.54	21.87	16.98	13.64	10.83
35°C	38.01	30.19	23.17	18.62	14.62
40°C	45.70	36.30	27.86	22.38	17.74

Table 1: Specific rate constant $k \times 10^3$ (dm³/mole/mint) values of alkali catalyzed Hydrolysis of Ethyl-Cinnamate in water-Acetone.

Temp in °C	3+Logk _D					
		D=60	D=55	D=50	D=45	D=40
	10 ³ /T	30%	40%	50%	60%	70%
20°C	3.412	1.120	1.040	0.970	0.890	0.790
25°C	3.355	1.260	1.90	1.105	1.045	0.970
30°C	3.300	1.380	1.390	1.240	1.165	1.095
35°C	3.247	1.570	1.485	1.400	1.320	1.235
40°C	3.195	1.665	1.585	1.505	1.425	1.345

Table 2: 3+Logk_D Value against 10³/T, Water- Acetone System.

Dielectric constant(D)	D=40	D=45	D=50	D=55	D=60
E _{exp} in KJ/mole	52.43	51.30	50.82	48.46	47.28

Table 3: Values of Iso-Dielectric Activation Energy (water-Acetone media).

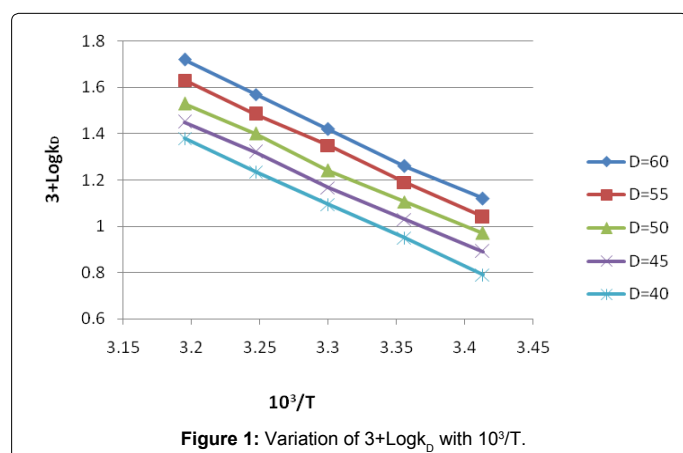


Figure 1: Variation of 3+Logk_D with 10³/T.

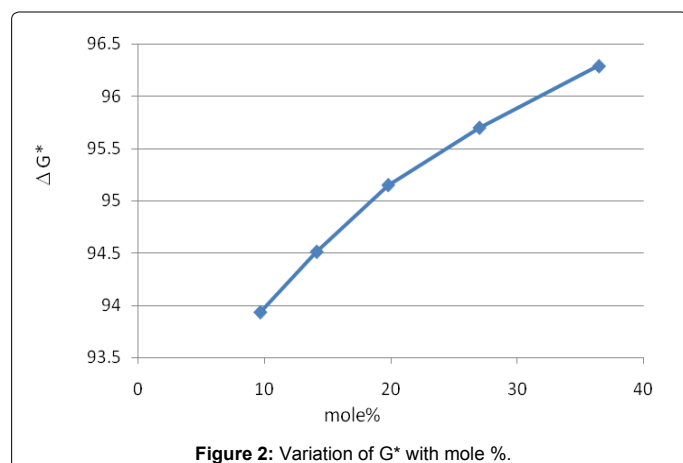


Figure 2: Variation of G* with mole %.

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

It may be inferred that the enhancement in the value of ΔG^* with simultaneous depletion in ΔH^* and ΔS^* value is only possible when the quantitative depletion in the value of ΔS^* is less than that found in the values of ΔH^* and from this fact, it is concluded that base catalyzed hydrolysis of Ethyl Cinnamate in water-acetone media is Enthalpy dominating and Entropy controlled. In another word, it may also be inferred that in presence of acetone in the reaction media activate the Enthalpy and control over the Entropy of the reaction.

The change found in the value of three thermodynamic activation parameters also support the fact that initial state of the reaction is desolvated and the transition state is solvated in the similar ways as recently reported [13-15]. The small but considerable increase in ΔG^* as shown in Table 3 and non-linear variation in ΔS^* curve with mole % of acetone shown in Figures 3 and 4 are indication of specific solvation taking place in the process of activation according to Seville and Hudson [13]. To explain the solvent effect on the thermodynamic parameters these three values namely ΔG^* , ΔH^* and ΔS^* were plotted against mole % of acetone in reaction shown in Figures 2-4 respectively. The non-linear variation in ΔH^* and ΔS^* give information specific solvation taking place in water-acetone as reported by Saviil et al. [13].

Solvent effect on the iso- dielectric activation energy of activation

From the slope of Arrhenius plot (obtain from interpolation of logk_D value against 10³/T at constant D of reaction media), the value of Iso dielectric activation energy of reaction have been evaluated and represented in Table 2. It is obvious that E_D value goes on decreasing from 52.43 to 47.28 KJ/mole with increasing in D value of water - Acetone media, is similar trend to recent finding (Figure 1) [14].

Evaluation of Iso-kinetic temperature and solvent-solute interaction

In the light of Barclay and Butler [15] relationship between Enthalpy and Entropy of Activation, which is as follows

$$\delta m (\Delta H^*) = \beta \delta m (\Delta S^*)$$

It is straight-line equation representing the relationship between Enthalpy and Entropy of Activation. β is the Iso-kinetic temperature. From the data available in the Table 4 the plot of ΔH^* and ΔS^* in the solvent system in Figure 5 and from the slope of straight line, the value of Iso-kinetic temperature was calculated to be 244 (water-acetone) and which is less than 300. From the value of Iso-kinetic temperature which is much less than 300, it is concluded that there is slow change in the structure of the reactant or in the solvent or in due to weak interaction between solvent and solute present in the reaction media in similar way as reported by Lefler [16] Our this conclusion has been recently supported (Figures 2-5) [17].

Conclusion

The result of this work indicate that the rate of hydrolysis of Ethyl cinnamate decreasing trend at all temp witch appear that transition state is more desolvated than initial state. The enhancement in the value of and ΔG^* with simultaneous depletion in ΔH^* ΔS^* for the hydrolysis ethyl inanimate in water- acetone is enthalpy dominating and Enthalpy control. The linear plots obtained by plotting logk as function of D represent the different electrostatic interaction for the ion-dipole as well as dipole-dipole reaction. The much less value (>300) of iso kinetic Temps indicate weak interaction between solvent and solute.

% of Me-OH	Mole %	ΔH^\ddagger in KJ/Mole	20°C		25°C		30°C		35°C		40°C	
			ΔG^\ddagger	$-\Delta S^\ddagger$	ΔG^\ddagger	$-\Delta S^\ddagger$	ΔG^\ddagger	$-\Delta S^\ddagger$	ΔG^\ddagger	$-\Delta S^\ddagger$	ΔG^\ddagger	$-\Delta S^\ddagger$
30%	9.65	42.41	92.09	169.55	93.01	169.79	93.93	170.03	94.59	169.41	95.87	170.79
40%	14.11	41.42	92.66	174.88	93.58	175.03	94.51	175.21	95.24	174.74	96.37	175.55
50%	19.77	39.88	93.19	181.94	94.10	181.94	95.15	182.40	95.92	181.94	97.06	182.68
60%	26.99	38.99	93.70	186.72	94.70	186.94	95.70	187.16	96.48	186.65	97.63	187.34
70%	36.45	35.90	94.26	199.18	95.25	199.16	96.29	199.30	97.11	198.73	98.24	199.16

Table 4: Thermodynamics Activation Parameters of the Reaction in Water- Acetone Media (ΔH^\ddagger and ΔG^\ddagger in KJ/Mole, ΔS^\ddagger in J/K/Mole).

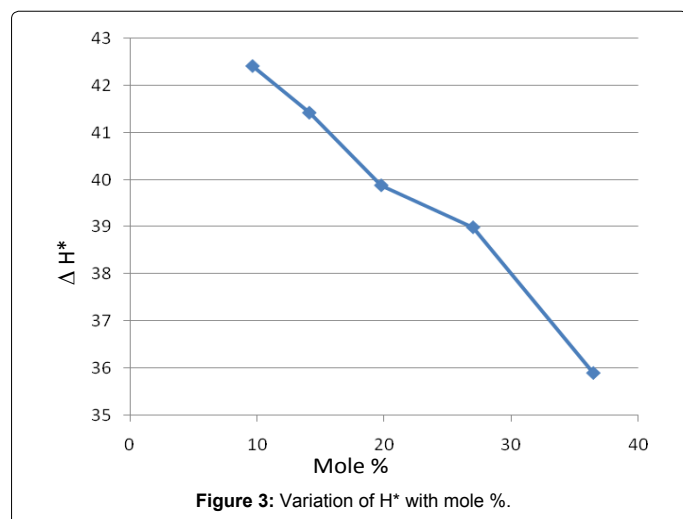


Figure 3: Variation of H^\ddagger with mole %.

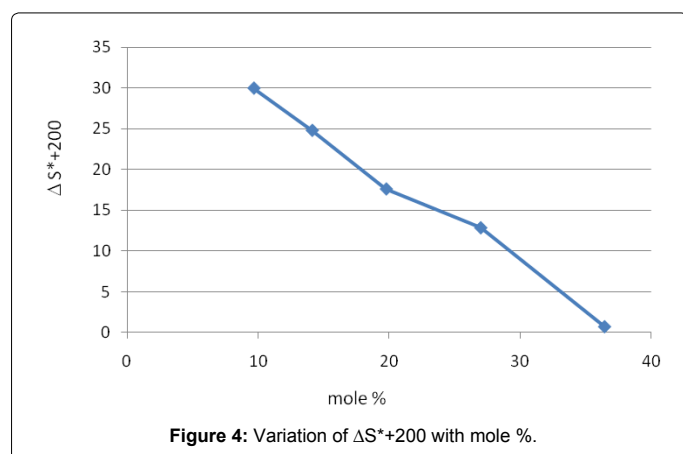


Figure 4: Variation of $\Delta S^\ddagger + 200$ with mole %.

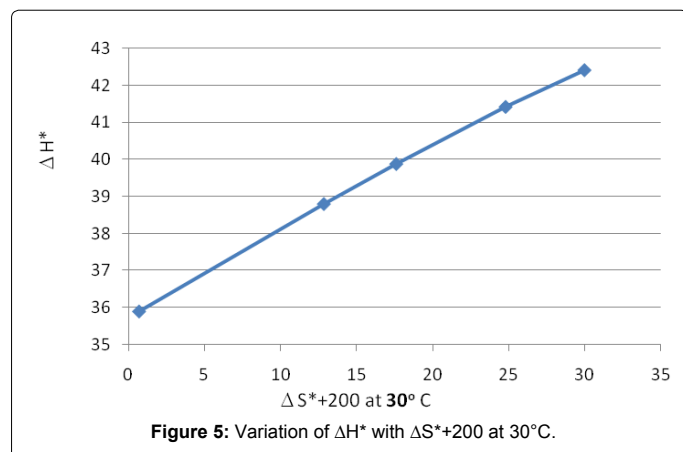


Figure 5: Variation of ΔH^\ddagger with $\Delta S^\ddagger + 200$ at 30°C.

Acknowledgment

My special gratitude to my supervisor Prof. Singh RT for his proper guidance and thanks to my friend Dr Ajit, Dr. Parag and Mr. Tiwari LK for his cooperation during preparation of this content. I am Thankful to Mrs Rolly Gupta & Miss Akansha for typing assistance.

Reference

- Sharma S, Ramani J, Bhalodia J, Vyas B (2013) Kinetic study of specific base catalyzed hydrolysis of ethyl acrylate in water-ethanol binary system. Russian J Phy Chem A 87: 730-736.
- Al-Jallal NA, Ismail AM (2012) Solvent Effects on the Kinetics of Amide Bond Cleavage in p-Chloro and p-Bromo Oxazolinones in Acetonitrile–Water Mixtures. J Solut Chem 41: 2154-2163.
- Fathalla MF (2011) Kinetics of the Reaction of 2-Chloro-quinoxaline with Hydroxide Ion in ACN–H₂O and DMSO–H₂O Binary Solvent Mixtures. J Solut Chem 40: 1258-1270.
- Singh AK (2017) The influence of solvent on the solvolysis of Ethyl cinnamate in water–Acetone mixtures. Int Res J Multidisc Stud 3: 79-82.
- Wynne-Jones WF, Eyring H (1935) The absolute rate of reactions in condensed phases. J Chem Phys 3: 492-502.
- Glasston S, Laidler KJ, Eyring H (1941) The theory of rate process. Mc Graw-Hill Newyork.
- Yagil G, Anbar NJ (1963) Classics in solid phase synthesis. J Am Chem Soc 85: 2149-2154.
- Tommila E (1955) Influence of solvent on reaction velocity. Acta Chem Scand 9: 957-988.
- Cleave NJ (1935) Soumen Kemi 45B pp: 79-80.
- Singh AK (2015) A kinetic study of solvent effect on thermodynamic activation parameter on alkali catalysed solvolysis of methyl salicylate in water-DMF media. Int J Adv Res Innvat 3: 547-549.
- Elsomogy MM, Abu Elamayem MS, Mussa, MNH (1975) Z Physik chem (Neuetold) 94: 69.
- Singh AK (2016) Solvolysis rate and activation parameters of ethyl acetate in mixed dipolar organic solvent system-A solvent effect. Int J Res Appl Sci Eng Technol 4: 706-710.
- Saville BJ, Hudson (1955) J Chem Soc 4114.
- Singh RT (2013) Kinetic study on the dielectric effect of water-t-butanol media on solvolysis of caproate ester. Napier Indian Advance Research J Sci 12: 78-88.
- Barclay L, Butler JAV (1938) Entropy of solution. J Am Chem Soc 34: 1445.
- Lefler JE (1955) The Enthalpy- Entropy relation and implication for organic chemistry. J Org Chem 20: 1201.
- Singh AK (2015) A kinetic study of solvent effect on thermodynamic activation parameter on alkali catalyzed solvolysis of methyl salicylate in water-DMF media. International conference of advance research and innovation. pp: 211-213.