

SOLVENT EFFECT ON THE ENTHALPY AND ENTROPY OF ACTIVATION FOR CINNAATE IN MIXED SOLVENT SYSTEM

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ABSTRACT

The concern for the presence of a wide variety of contaminants in the environment calls for development and assemblage of information about their behavioral characteristics so that appropriate strategies can be adopted to either prevent or minimize their adverse impacts on human welfare and natural resources. This information is especially warranted for toxic chemicals that persist for extended periods of time in the environment. When chemicals enter the environment, they are usually not confined to a specific location but rather are in dynamic motion either within a medium or across the adjacent media. The propensity for a contaminant to move into and distribute itself between the media (or phases) is determined by its physical and chemical properties and environmental factors and variable. The rate of alkaline hydrolysis of ethyl cinnamate was measured over the temperature range of 40°C to 80°C in water-acetone mixture at different composition 20 to 60% (v/v). The influence of solvent variation on reaction rate was examined in term of changes in the Activation parameter. Depletion of ΔH^ and ΔS^* value with simultaneous increase in ΔG^* of the reaction in reaction media, reveals that the reaction is Enthalpy domination and Entropy controlled. The Iso- dielectric activation energy (ED) of reaction was found to decrease from 55.43 to 45.28. The Values of Iso-kinetic Temperature which is less than 400, 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.*

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 20 to 60% (v/v) at five different temperature ranging from 40°C to 80°C at regular interval of 25°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 $\log k_D$ 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 in reaction media, the value $\log k$ tabulated in Table 1. The decrease observed in specific rate constant with increasing concentration of organic solvent is probably due to depletion of Dielectric constant of media and salvation change taking place in media [4].

Law Of Thermodynamic

The first law of thermodynamics is a consequence of the principle of conservation of energy: that is, that heat, kinetic energy, potential energy, and electrical energy are different forms of energy that can be interconverted but can be neither created nor destroyed. Consider any system

enclosed in a vessel that can change its volume and exchange heat with its surroundings but is impervious to the passage of matter. We postulate a property called the *internal energy* of the system, E . We will be concerned with the change in E and not with its absolute value. If the system absorbs an amount of heat q with no other changes, the conservation of energy requires that its internal energy increase by the amount of q ; conversely, the internal energy will decrease by the amount of q if an amount of heat q is released to its surroundings. Similarly, if the system does work w on its surroundings with no other changes, its internal energy will decrease by the amount of w . If the system both exchanges heat and does work, the change in internal energy is then

$$\Delta E = q - w \quad (1.1)$$

where q is here taken as positive for heat absorbed by the system and w as positive for work done by the system. The first law also implies that E is a *state function*: that its magnitude is solely dependent on its state variables (e.g., temperature, pressure, and volume). For any series of processes that end with a return to the original state variables, $\Delta E = 0$. For a constant-pressure system involving only the work of expansion and contraction (i.e., no electrical work), w equals $P\Delta V$, where P is the (constant) pressure and ΔV is the (finite) change in volume. In this case, the change in E is therefore

$$\Delta E = q - P\Delta V \quad (1.2)$$

If one defines a new state function, H , called *enthalpy*, as

$$H = E + PV \quad (1.3)$$

then the change in H at constant pressure will be

$$\Delta H = \Delta E + P\Delta V \quad (1.4)$$

A comparison of Eqs. (1.2) with (1.4) leads to

$$\Delta H = q \text{ for a constant-pressure process} \quad (1.5)$$

The enthalpy is therefore a useful state function for describing the heat exchange at constant pressure.

Solvent effect and thermodynamic activation parameters

The thermodynamics Activation parameter such as Enthalpy of Activation (ΔH^*), Entropy of Activation (ΔS^*) and free energy of Activation (ΔG^*), 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 in ΔG^* value in case of water-acetone increases from 95.09 to 97.26 KJ/mole with change of proportion of solvents from 20% to 60% at 40°C. Though the enhancement is not large, however it is quite considerable. 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^* 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^* with mole % in the solvent are non-linear and increase smoothly with gradual addition of the solvent.

This finding is indicative of salvation 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^* , ΔG^* and ΔS^* , the value of ΔH^* and ΔS^* goes on decreasing with simultaneous increase in G^* values with increasing proportion of acetone at all the temperature of the reaction, i.e., from 40°C to 80°C. From the fundamental thermodynamic equation

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

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 indication of specific salvation 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. The non-linear variation in ΔH^* and ΔS^* give information specific salvation 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 $\log k_D$ 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 ED value goes on decreasing from 55.43 to 45.28 KJ/mole with increasing in D value of water – Acetone media.

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 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 [16,17].

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 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 $\log k$ 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.

REFERENCE

1. 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.
2. 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.

3. 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.
4. Singh AK (2017) The influence of solvent on the solvolysis of Ethyl cinnamate in water–Acetone mixtures. *Int Res J Multidisci Stud* 3: 79-82.
5. Wynne-Jones WF, Eyring H (1935) The absolute rate of reactions in condensed phases. *J Chem Phys* 3: 492-502.
6. Glasston S, Laidler KJ, Eyring H (1941) The theory of rate process. Mc Graw- Hill Newyork.
7. Yagil G, Anbar NJ (1963) Classics in solid phase synthesis. *J Am Chem Soc* 85: 2149-2154.
8. Tommila E (1955) Influence of solvent on reaction velocity. *Acta Chem Scand* 9: 957-988.
9. Cleave NJ (1935) *Soumen Kemi* 45B pp: 79-80.
10. Singh AK (2015) A kinetic study of solvent effect on thermodynamic activation parameter on alkali catalised solvolysis of methyl salicylate in water-DMF media. *Int J Adv Res Innvat* 3: 547-549.
11. Elsemogy MM, Abu Elamayem MS, Mussa, MNH (1975) *Z Physik chem (Neuetold)* 94: 69.
12. 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.
13. Saville BJ, Hudson (1955) *J Chem Soc* 4114.
14. 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.
15. Barclay L, Butler JAV (1938) Entropy of solution. *J Am Chem Soc* 34: 1445.
16. Lefler JE (1955) The Enthalpy- Entropy relation and implication for organic chemistry. *J Org Chem* 20: 1201.
17. 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 confrence of advance research and innovation*. pp: 211- 213.

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

Temp in °C	% of ACETONE				
	30%	40%	50%	60%	70%
20°C	16.66	12.22	11.00	9.12	7.45
25°C	22.89	18.59	15.48	11.59	9.49
30°C	28.54	20.87	15.98	11.64	12.83
35°C	39.01	36.19	27.17	19.62	16.62
40°C	40.70	35.30	26.86	23.38	18.74

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

Temp in °C	10 ³ /T	3+Logk _D				
		D=60	D=55	D=50	D=45	D=40
		30%	40%	50%	60%	70%
20°C	3.41	2.12	1.04	0.97	0.89	0.79
25°C	3.35	1.26	1.90	1.10	1.04	0.97
30°C	3.30	2.38	1.390	1.24	1.16	1.09
35°C	3.24	1.57	1.485	1.40	1.32	1.23
40°C	3.19	1.66	1.585	1.50	1.42	1.34

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

Dielectric constant(D)	D=40	D=45	D=50	D=55	D=60
E _{exp} in KJ/mole	55.43	53.30	52.82	49.46	48.28