Application of Singh-Jha Equation in the Evaluation of b^* Parameter of Laidler-Landskroener Equation in the Hydrolysis of Vinyl Acetate

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Abstract: Singh-Jha method is applied to calculate b^* of Laidler-Landskroener equation, the distance of closed approach of solvent molecules to the activated complexes in alkaline hydrolysis of vinyl acetate. This method is applied to alkaline hydrolysis of vinyl acetate in water enriched ethanol between 30 °C and 35 °C. The rate of hydrolysis decreases with the increase of content of organic solvent at both temperatures. The size of transition state was found to be large as compared to the initial state. The b^* was found to be 3.7693 Å which is in agreement with the values obtained earlier.

Keywords: Solvent effect, b^* parameter, Alkaline hydrolysis, Vinyl Acetate.

Introduction

Many hypothetical models were assumed to arrive to a complicated mathematical treatment to calculate the size of the active group of activated complex (b^*) for an ion-dipole type of reactions by Laidler-Landskroener¹. Among the various theoretical expressions, relating rate constant with the properties of solvents and reactants, the Laidler and Landskroener equation² is widely accepted. The equation for ion-dipole type of bimolecular reaction in solution where the transition state is much more polarized than the initial state can be expressed as follows;

$$\log k = \log k_0 + \frac{1}{2.303} \frac{e^2}{2kT} \left(\frac{1}{b_A} - \frac{1}{b^*} - \frac{3G^*}{2b^{*3}} \right) \frac{1}{D} + \frac{1}{2.303} \frac{e^2}{2kT} \left(\frac{1}{b_A} - \frac{1}{b^*} - \frac{3G^*}{4b^{*3}} \right) \quad (1)$$

The Laidler and Landskroener method for evaluating b^* , the size of the active group of activated complex for a bimolecular reaction is applicable only when the transition state is

more polarized. A more general method for calculating b^* in case of above mentioned reactions, irrespective of the polarity of the transition state have been suggested by Singh-Jha equation². Singh-Jha equation is applicable for variation of specific rate constant for an ion-dipole type of bimolecular equation in which transition state may or may not be polarized and slope of $\log k$ against $1/D$ may be positive or negative.

The applicability of the above equation has been tested by several authors^{3,4} by calculating the value of b^* for several ion-dipole type of bimolecular reactions yielding a negative slope for $\log k$ against $1/D$.

However, the computation suffers from an arbitrary assumption about the dielectric constant of ideal solution and the equations have not been applied for those ion-dipole type of reactions in which a linear relationship of $\log k$ against $1/D$ yields a negative value. Therefore the present work is undertaken with a view to apply an equation for the variation of specific rate constant for an ion-dipole type of bimolecular reaction in which the transition state is being polarized and the slope of $\log k$ against $1/D$ is being negative.

Experimental

Systronics conductometer (model-306) with cell constant 1 ± 0.01 was used. The instrument was standardized with 0.01 M KCl solution. The total volume and concentration of all used chemicals was kept constant throughout the study. Hydrolytic reaction were carried out at 30 °C and 35 °C using the help of an electrically controlled high precision water bath Ca. No. MSW-274 with the readability of 0.01 °C.

The ester used was obtained from Merck make and the ethanol was purified by standard procedure⁵. The procedure followed for the conductometric measurement was similar to that used by Charles and Muller⁶. Standard solution of NaOH (0.02 M) and vinyl acetate (0.02 M) were proposed in solvent mixture of ethanol varying from 10-50% in conductivity water. The above solutions in a particular solvent composition were thermostated in a bath controlled within ± 0.1 °C. After mixing equal volume of both the solution, the rate constants were studied by conductivity measurements. The values of specific rate constant, k were found within the experimental error range (± 0.05) with the values of k obtained from plot of $(C_0 - C_t / C_t - C_\infty)$ against t . The specific rate constant values at 30 °C and 35 °C are shown in Table 1.

Results and Discussion

For the evaluation of b^* parameter the following equation which was proposed by Singh and Jha is as given:

$$\frac{1}{b_A} - \frac{1}{b^*} = \frac{1}{A} \left[X - \frac{1+\alpha}{\alpha} (X+Y) \right] \quad (2)$$

Where, x is the product of the slope of the $\log k$ vs. $1/D$, A is $\frac{1}{2.303} \frac{e^2}{2k}$ b_A is the size of the reactant ion, α is the half of the dielectric constant (D), e is the electron charge, b^* is the size of the active group of the activated complex in the reaction, Y is the parameter whose mean value between the two temperatures T_1 and T_2 can be determined by the equation (2)

$$\log \frac{k_1}{k_2} = \left[\frac{X_1}{D_1 T_1} - \frac{X_2}{D_2 T_2} \right] + Y \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (3)$$

Using this equation, the size of the active group of the activated complex (b^*) have been calculated. This equation has been used by S. Kumar and his coworkers⁷. The specific rate

calculated in various solvent mixtures at 30 °C and 35 °C are shown in Table 1. The table also includes the dielectric constant values extrapolated from the curve using the data of Wolford⁸.

Table 1. Specific constant values of vinyl acetate in water-ethanol mixture.

v/v, % ethanol-water	K, specific rate constant		Dielectric constants of solvent mixture at	
	30 °C	35 °C	30 °C	35 °C
10	14.71	16.44	71.23	69.54
20	12.69	14.72	65.53	63.87
30	10.95	12.71	59.68	58.20
40	8.55	10.15	53.78	52.43
50	6.90	8.35	47.84	46.57

Results show that the rate constant values are gradually decreasing with the gradual addition of ethanol in the reaction medium at both temperatures of study. This is in accordance with quantitative predictions of Houghes and Ingold⁹ theory. Alkaline hydrolysis of ester being an ion-dipole type of reaction, the transition state is supposed to be highly polar and therefore, its formation will be disfavored with the increase of organic co-solvent content on account of progressive decrease in the dielectric constant of the medium resulting in decrease in the rate constant.

In case of alkaline hydrolysis of vinyl acetate in water enriched ethanol, the graph of log k against 1/D was found to be linear and the value of X/T at 30 °C and 35 °C calculated from the slope were -48.34 and -42.39 respectively. The values of Y between 30 °C and 35 °C evaluated with the help of equation (2) are shown in Table 2. The size of OH⁻ ion (b_A) in aqueous medium was calculated earlier and was found to be 3.69 Å from its molar volume¹⁰ and the size of H₃O⁺ in water.

Table 2. Values of X, Y and b^* in water-ethanol mixtures.

v/v, % Ethanol-water	Values of Y	Value of X/T at 30 °C	b^* in Å at 35 °C
10	412.00		3.6954
20	149.32		3.8022
30	317.00	-48.34	3.7593
40	247.00		3.8022
50	335.00		3.7878

The average value of b^* found here is to 3.7693 Å, it means the distance of closest approach of a solvent molecule to the seat of reaction is 3.7693 Å, it is unreasonable. Thus the value of b^* is a very important parameter for predicting solvent effect, appears to be quite conventional.

According to Kirkwood theory^{11,12}, these radii should not correspond to overall radii but should be effective radii related to size of active groups in the complex molecules. Therefore the essential factor is closeness of approach of the solvent molecules to the seat of reactions. It is quite possible that solvent sheath over the OH⁻ ion present in the bulk is removed in the transition state and similar to the spreading of the charge, the solvent sheath too spreads over the transitions states.

Again, the solvation of transition state will be much less in comparison to reactant ion due to the decrease in the charge density. As the size of bare OH⁻ ion is 1.4 Å, the effective size of the transition state species, defined as the distance of closed approach of a solvent molecule to seat of reaction is found to be 3.7693 Å is unreasonable.

The distance of C.... O bond reported¹³ is 1.43Å. It is therefore quite reasonable that C....OH bond which is being formed in transition state due to attack of OH⁻ ion on the carbon group of ester may be between 2 to 4Å in case of simple ester hydrolysis.

Conclusion

This methods for calculating b* parameter are important for predicting the solvent effects. In ion-dipole type of reactions where transition state is less polarized or of reverse polarity, the Laidler –Landskroener method may not be applied for calculating b* whereas, Singh-Jha equation can be applied easily. So Singh- Jha equation is successfully applied to study the b* parameter for alkaline hydrolysis of vinyl ester.

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