

## Calculation of $b^*$ of Laidler and Landskroener Equation for Ion-Dipole Type of Reactions

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The Laidler and Landskroener method for evaluating  $b^*$ , the size of the activated complex in a bimolecular reaction, is applicable only when the transition state is polarized. A more general method for calculating  $b^*$  in case of above mentioned reactions irrespective of polarity of transition state has been suggested. The method has been applied in alkaline hydrolysis of ethyl picolinate in acetone-water mixture at temperatures 25°C, 30°C, 35°C and 45°C. The  $b^*$  was found to be between 5 Å to 6 Å.

### INTRODUCTION

In respect of ion-dipole type bimolecular reactions where transition state is more polarized than the initial state, the Laidler and Landskroener equation<sup>1</sup> is most widely accepted.

Attempts have been made to calculate the size of activated complex ( $b^*$ ) for several ion-dipole type bimolecular reactions. The method of calculation of  $b^*$  has been refined and simplified by proposing a pair of equations by authors<sup>2</sup>. Our present work is to test the applicability of proposed equation in cases where a plot of  $\log K$  against  $1/D$  results with negative slope. With wide range of researches on solvent effect<sup>3-6</sup>, it is now recognised that the action of non-aqueous component of a mixture is more than simple diluent on its dielectric properties. Therefore, the authors have selected to study the alkaline hydrolysis of ethyl picolinate in acetone-water mixture in order to explore the pronounced specific effects of the solvent mixture and to apply the available data for the evaluation of  $b^*$ .

### EXPERIMENTAL

The chemicals and procedures for this experiment have already been described<sup>7</sup>. The rate constant values were evaluated from the equation

$$\Delta_t = \Delta_\infty + \frac{1}{ak} \cdot \frac{\Delta_0 - \Delta_t}{t}$$

where  $\Delta_0$  is the initial conductivity before addition of ester to the alkali,  $\Delta_t$  the conductivity at time  $t$ ,  $\Delta_\infty$  the conductivity when the ester is completely

hydrolysed and  $a$  is the mole concentration of the alkali. The rate constant value was calculated from the slope of the plot of  $\Delta_t$  against  $\frac{\Delta_0 - \Delta_t}{t}$ .

The specific rate constants calculated in aquo-acetone mixture at 25°C, 30°C, 35°C and 45°C are shown in Table-1. The table also includes the dielectric constant values calculated from the data of Woford-Akerlof's equation.

TABLE-1  
SPECIFIC RATE CONSTANTS ( $k$  in  $\text{dm}^3 \text{mole}^{-1} \text{min}^{-1}$ )  
AND DIELECTRIC CONSTANT (D) VALUES IN  
AQUO-ACETONE MEDIA

%		25°C	30°C	35°C	45°C
10	K	17.8	25.1	35.5	70.8
	D	73.9	72.3	70.8	67.6
20	K	13.2	18.6	25.7	50.1
	D	68.9	67.3	65.8	62.8
30	K	11.2	15.9	21.4	39.8
	D	63.6	62.3	60.8	58.0
40	K	10.0	13.5	18.2	33.1
	D	59.2	58.3	55.4	52.8
50	K	8.5	11.2	15.1	26.3
	D	53.3	52.3	49.4	47.2

## RESULTS AND DISCUSSION

The Laidler-Landskroener equation is based on the assumption that the change in the solvent composition results in the change of activity coefficient. The activity coefficient expression has been given by Kirkwood<sup>8,9</sup> which is as follows:

$$\ln Y = \frac{e^2}{2KT} \left[ \frac{1}{D} \left\{ \frac{z^2}{b} + \frac{3G}{2b^3} \right\} - \left\{ \frac{z^2}{b} + \frac{3G}{2(1+\alpha)b^3} \right\} \right] \quad (1)$$

where  $G$  is a number depending on the distribution of charges and proportional to dipole moment and  $\alpha$  is half of the dielectric constant of solute. The other terms have their usual significance.

Using a bimolecular reaction of the type  $A + B \rightarrow AB^*$ , the rate constant is expressed as

$$\ln K = \ln K_0 + \ln \frac{Y_A Y_B}{Y_{AB^*}} \quad (2)$$

Taking the help of the equation (1), equation (2) takes the form

$$\log K = \log K_0 + \frac{1}{2.303} \cdot \frac{e^2}{2KT} \left[ \left\{ \left( \frac{1}{b_A} - \frac{1}{b^*} + \frac{3}{2} \frac{\Sigma G}{b^3} \right) \frac{1}{D} \right\} - \left\{ \frac{1}{b_A} - \frac{1}{b^*} + \frac{3}{2(1+\alpha)} \frac{\Sigma G}{b^3} \right\} \right] \quad (3)$$

where

$$\Sigma \frac{G}{b^3} = \frac{G_A}{b_A^3} + \frac{G_B}{b_B^3} - \frac{G^*}{b^{*3}}$$

and it is proportional to change in polarisation of the reactants due to the formation of transition state.

Considering the equation (3) in general form,

$$\log K = \log K_0 + \frac{X}{TD} + \frac{Y}{T} \quad (4)$$

where

$$X = \frac{1}{2.303} \cdot \frac{e^2}{2K} \left( \frac{1}{b_A} - \frac{1}{b^*} + \frac{3}{2} \Sigma \frac{G}{b^3} \right)$$

and

$$Y = -\frac{1}{2.303} \cdot \frac{e^2}{2K} \left( \frac{1}{b_A} - \frac{1}{b^*} + \frac{3}{2(1+\alpha)} \Sigma \frac{G}{b^3} \right)$$

Rearranging the expressions for  $X$  and  $Y$  and putting  $A = \frac{1}{2.303} \frac{e^2}{2K}$  we have

$$\frac{1}{b_A} - \frac{1}{b^*} + \frac{3}{2} \Sigma \frac{G}{b^3} = \frac{X}{A} \quad (5)$$

and

$$\frac{1}{b_A} - \frac{1}{b^*} + \frac{3}{2(1+\alpha)} \Sigma \frac{G}{b^3} = \frac{-Y}{A} \quad (6)$$

Substituting the value of  $\Sigma \frac{G}{b^3}$  in equation (5) we have

$$\frac{1}{b_A} - \frac{1}{b^*} = \frac{1}{A} \left[ X - \frac{(1+\alpha)}{\alpha} (X+Y) \right] \quad (7)$$

The value of  $X$  can be obtained from the slope of  $\log K$  against  $1/D$  and the mean value of  $Y$  between two temperatures can be determined from the expression

$$\log \frac{K_1}{K_2} = \left( \frac{X_1}{D_1 T_1} - \frac{X_2}{D_2 T_2} \right) + Y \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8)$$

The terms with subscripts 1 and 2 represent their values at temperatures  $T_1$  and  $T_2$ .

For the alkaline hydrolysis of ethyl picolinate in aquo-acetone media, the graph of  $\log K$  against  $1/D$  was found to be almost linear. The values of  $X/T$  and  $Y$  are calculated from the slopes at temperatures 25°C, 30°C, 35°C and 45°C. The values of  $Y$  are evaluated with the help of the equation (8). The size of  $\text{OH}^-$  ion ( $b_A$ ) in aqueous medium was calculated from its molar volume<sup>10</sup> and the size of  $\text{H}_3\text{O}^+$  ion in water. Thus, using the values of  $X/T$ ,  $Y$  and  $b_A$ , the values of  $b^*$  were calculated with the help of equation (7) and are given in Table-2.

TABLE-2  
VALUES OF  $b^*$  FOR ALKALINE HYDROLYSIS OF  
ETHYL PICOLINATE IN AQUO-ACETONE MEDIA

Temperature °C	$b^*$ (Å)
25	5.45
30	5.42
35	5.36
45	5.27

According to Kirkwood theory, these radii should not correspond to the overall radii but these should be effective radii related to the size of the active groups in the complex molecules. The essential factor is the closeness of the approach of the solvent molecules to the seat of reactions.

It is reasonable that the new C—OH bond which is formed in the transition state due to attack of  $\text{OH}^-$  ion on the carbonyl group of the ester may lie between 5 Å to 6 Å in case of ethyl picolinate ester hydrolysis. Thus, the method proposed for the evaluation of  $b^*$  appears to be quite convincing. The  $b^*$  values decrease with increase in temperatures. It justifies the fact that with the increase in temperature, there is randomness of the system and the solvation sheath is likely to decrease. Further investigations are in progress to apply the method suggested in various types of ion-dipole reactions in different solvent media.

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