

## **SOLVENT EFFECT ON MECHANISM OF ALKALINE HYDROLYSIS OF PHENYL ETHYL BENZOATE**

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### **ABSTRACT**

Solvents play an important role in determining chemical reactivity. Apart from providing a physical environment for the reaction, solvents in a number of elementary processes exert a chemical effect as well. Therefore, a solvent can change not only the rate of a reaction but its mechanism also. The kinetics of alkaline hydrolysis of phenyl ethyl benzoate was studied in water–tert. butyl alcohol media of different compositions at different temperatures to arrive at a conclusion about the reaction mechanism. The enhancement in specific rate constant values and change in other activation parameters with increasing proportion of t-butyl alcohol in the reaction medium have been explained on the basis of lowering of dielectric constant of the medium and relative desolvation of initial state as well as greater solvation of transition state. The positive values of molar polarisation energy change indicates that the initial state is more polar than transition state. The size of the transition state was found to be large compared to the size of the initial state. The reaction was proposed to proceed through acyl–oxygen bond cleavage (B<sub>AC</sub>2)

**Key word :** Alkaline hydrolysis, Phenyl ethyl benzoate, Solvent effect

### **INTRODUCTION**

Although several hydrolysis reactions have been studied in aquo–organic binaries, the influence of the solvent on the rate and mechanism of reactions in solution has not been interpreted satisfactorily. Kinetic studies provide valuable information about reaction mechanism, especially when work has been done over a wide range of conditions. The results have been interpreted on the basis of a number of parameters such as dielectric constant effect<sup>1</sup>, solvation effect<sup>2</sup>, etc. It is believed that these effects operate simultaneously. However, one effect predominates over the other depending on the nature of the solvent as well as type of reaction. Here, it must be emphasized that it is never possible to arrive at a firm conclusion about a reaction mechanism in solution. Recently, an attempt has been made to explain the solvent effect on the basis of change in polarisation energy expressed by the function  $\Sigma NGe^2/b^3$ . The experimental evaluation of the function for a reaction gives valuable evidence concerning the

influence of the solvent. However, much data and more studies are needed to predict the function from the knowledge of reactants and the medium.

In this context, it is proposed to study the alkaline hydrolysis of phenyl ethyl benzoate in water-tert.-butyl alcohol media.

## EXPERIMENTAL

The alkaline hydrolysis of phenyl ethyl benzoate was followed by the usual titration method using standard baryta solution. The rate constant values were obtained by using the equation for a second order reaction. The iso-composition activation energy,  $E^*$  was calculated using Arrhenius equation and plotting  $\log k$  against  $1/T$ . The activation parameters such as  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  were calculated by absolute rate theory,

$$k = \frac{k'}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R}$$

and plotting  $\log k$  against  $1/T$ .

The molar polarisation energy change  $\Sigma NGe^2/b^3$  was obtained by using the modified equation of Singh *et al*<sup>3</sup>

$$\Sigma NGe^2/b^3 = 4.094 RTA (1 - 1/D) - 1.8 E_D$$

The value of potential energy decreases due to activation

$$N \left( \frac{Z^2 e^2}{b_A} - \frac{Z^2 e^2}{b^*} \right)$$

and size of the transition state,  $b^*$  were also calculated using recent modified equation<sup>2,3</sup>

$$N \left( \frac{Z^2 e^2}{b_A} - \frac{Z^2 e^2}{b^*} \right) = 2.7 E_D - 1.53 RTA$$

## RESULTS AND DISCUSSION

The specific rate of alkali catalysed hydrolysis of phenyl ethyl benzoate in water-t-BuOH media ranging from 50 to 80% (v/v) of t-BuOH and at temperature 293 to 308 K has been found to increase with gradual increase in the proportion of the t-BuOH (Table 1). The enhancement in the rate of such reaction, where the transition state is more polar, should be faster in aprotic solvent than in protic solvent<sup>4</sup>. The increase in rate with decrease in dielectric constant of the medium is due to pronounced solvation effect. Since t-BuOH is poor anion solvator than water, therefore, it relatively desolvates the initial state and rate enhances, which is also supported by the decrease in value of activation parameters (Table 2). The decrease in  $\Delta E^*$  values must have been caused due to the greater desolvation of initial state as compared the transition state. The

role of water concentration in aquo-*t*-BuOH medium confirms that the reaction going on is bimolecular in nature<sup>5</sup>.

The plot of  $\Delta H^*$  against  $\Delta S^*$  (isokinetic plot) gave straight line with slope value of 325, which is in accordance with Leffer and Grunwald<sup>6</sup>.

The iso-dielectric activation energy,  $E_D$ , was obtained by plotting  $\log k_D$  against  $1/T$ . From the slope of plots,  $E_D$  values were found to increase with increasing dielectric constant (Table 3). It is indicative of the fact that here solvation effects play more dominant role than dielectric effect. The values of  $\Delta E^*$  and  $E_D$  were plotted against  $D$ . The variations of  $\Delta E^*$  and  $E_D$  are almost similar in nature. Elsemongy *et al.*<sup>7</sup> has compared the values of  $E_D$  and  $\Delta E^*$  and gave an expression correlating the two as

$$\Delta E^* = E_D - 2.3 b D R T^2 \left( \frac{d \ln k}{d D} \right)_T$$

where "b" is the slope of the plot  $\log k_D$  against  $1/T$ . From the plot, it is obvious that for all dielectric constant values,  $E_D$  is always higher than  $\Delta E^*$ . Kumar and Singh<sup>8</sup> also support this observation in hydrolysis of benzyl benzoate in the *t*-BuOH-water medium.

### Molar polarization energy change and size of transition state

Singh *et al.*,<sup>2</sup> have suggested a modified procedure to calculate the function  $\Sigma N G e^2/b^3$  from the solvent effect study. The corresponding values are given in Table 4. The molar polarization energy change was found to be positive confirming the earlier conclusion of more polar initial state than the transition state. The decreasing trend of the value with increasing temperature suggests greater desolvation of initial state.

The size of transition state ( $b^*$ ) which is in effective size of transition state anion was found to increase from 3.48 Å to 4.12 Å, which seems reasonable and acceptable as it is comparable to that reported by Singh *et al.*<sup>9</sup>.

### Potential energy decrease

The value of decrease in potential energy in activation process was positive at higher temperatures whereas it is -18.12 kJ at a lower temperature of 293 K (Table 4). This shows that in the solution and specially in alkaline hydrolysis of phenyl ethyl benzoate, the potential energy surface at the 'col' has a definite cavity at temperature greater than 298 K. The depth of the cavity depends upon the solvent composition as well as on temperature. The existence of such cavity in the potential energy surface may be taken as an indication of formation of unstable reaction intermediate<sup>10</sup>.



**Table 1. Specific rate constant, k for alkaline hydrolysis of phenyl ethyl benzoate in t-butyl alcohol–water media.**

t-BuOH Vol (%)	Temperature (K)			
	293	298	303	308
50	0.068	0.096	0.126	0.172
60	0.079	0.106	0.142	0.182
70	0.103	0.133	0.169	0.215
80	0.163	0.187	0.226	0.265

**Table 2. Activation parameters for alkaline hydrolysis of phenyl ethyl benzoate in t-butyl alcohol–water media.**

t-BuOH Vol (%)	$\Delta E^*$ in $\text{kJmol}^{-1}$	$\Delta H^*$ in $\text{kJmol}^{-1}$	$-\Delta S^*$ in $\text{kJmol}^{-1}$	$\Delta G^*$ in $\text{kJmol}^{-1}$			
				293 K	298 K	303 K	308 K
50	46.20	42.73	155.32	88.24	89.02	89.79	90.57
60	43.63	38.17	169.41	87.81	88.65	89.50	90.35
70	36.90	33.84	182.17	87.22	88.13	88.04	89.95
80	24.15	20.91	222.54	86.11	87.23	88.34	89.45

**Table 3. Iso-dielectric activation energy,  $E_D$** 

Dielectric Constant	24	28	32	36	40	44	48
$E_D$ in $\text{kJ mol}^{-1}$	16.68	19.85	26.49	32.06	40.41	42.86	44.51

**Table 4. Molar polarisation energy change,  $\Sigma NGe^2/b^3$ , size of the transition state,  $b^*$  and potential energy decrease.**

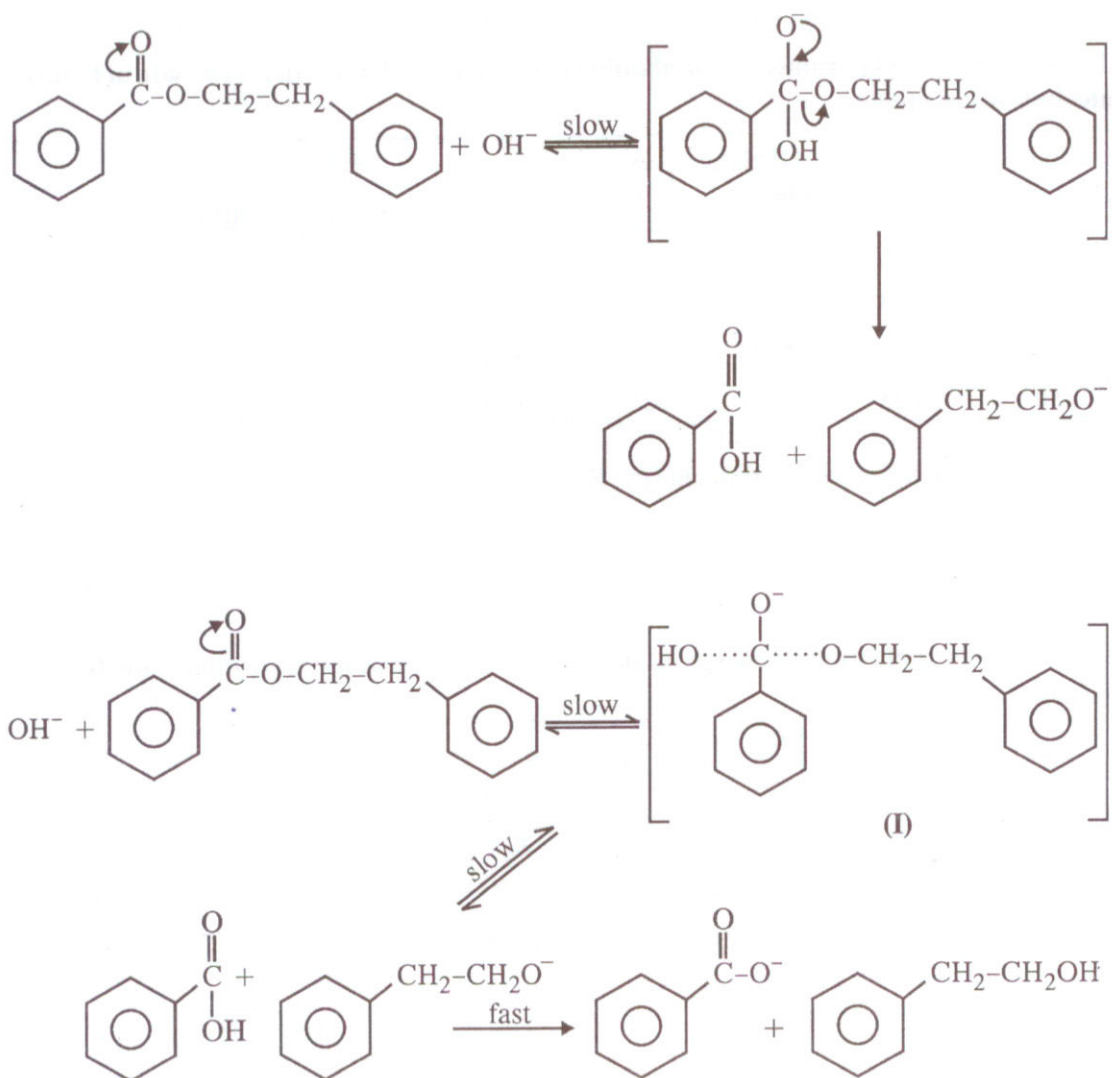
$$N \left( \frac{Z^2 e^2}{b_A} - \frac{Z^2 e^2}{b^*} \right) \text{ at } D = 36$$

Temperature in K	298	303	308	33
$\Sigma NGe^2/b^3$ in $\text{kJ mol}^{-1}$	216.23	137.81	98.95	62.81
$N \left( \frac{Z^2 e^2}{b_A} - \frac{Z^2 e^2}{b^*} \right)$ in kJ	-18.12	11.84	26.69	40.51
$b^*$ in Å	3.48	3.82	3.98	4.12

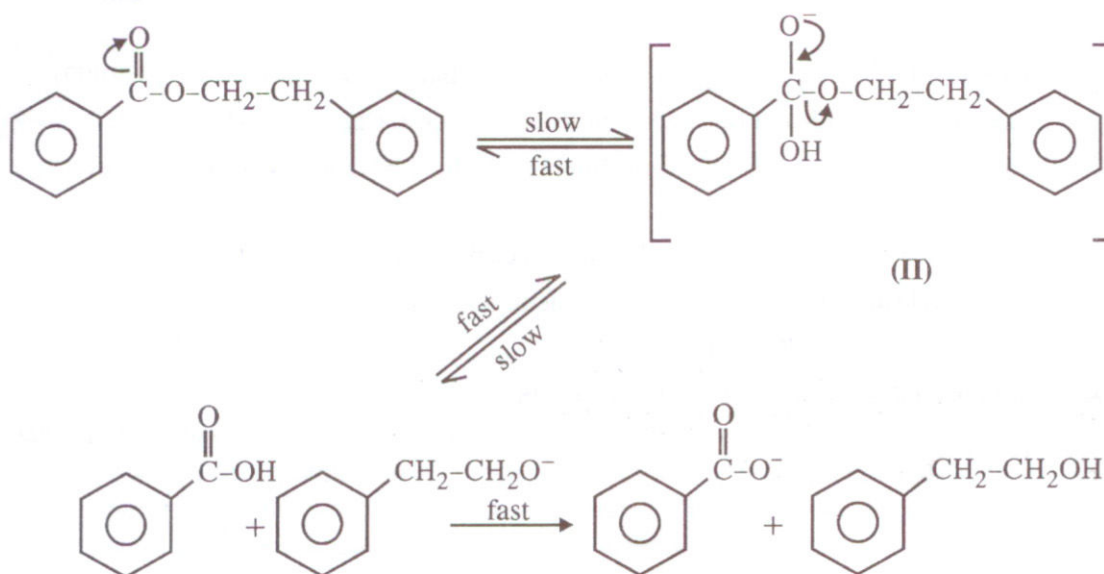
### MECHANISM

The most common mechanism for base catalysed hydrolysis of ester is  $S_N2$  i.e. the transition state constitutes one molecule of ester and one of the catalysing base. The cleavage of the ester may take place either at acyl-oxygen bond or alkyl-oxygen bond but several workers<sup>11,12</sup> have suggested the acyl-oxygen bond cleavage.

Several attempts were made to elucidate the mechanism, but only two have been suggested so far. The first mechanism is followed by the direct displacement at the carbonyl carbon atom analogous to the  $S_N2$  reaction.



The second mechanism is the addition–elimination mechanism in which the base first forms a covalent bond with the ester resulting in a tetrahedral intermediate (II) as:



The mechanism involving a tetrahedral intermediate has been supported by Bender<sup>13</sup>. Tetrahedral intermediate has a negative charge and is crowded. It is expected that the alkaline hydrolysis will be influenced by both, the polar and steric effects. Electron attracting group present in the acyl portion of the ester should, therefore, accelerate the rate. This fact has been verified experimentally for ethyl ester in water at 398 K<sup>14</sup>. Presence of bulky groups both in the acyl and alkyl portion of ester retards the reaction rate. In both the cases, progressive substitution of a heavier group lowers the hydrolysis rate. This is further supported by the  $E_S$  values, the steric substituent constants, because a large negative value of  $E_S$  corresponds to a bulky group, which results in a decrease in rate by alkyl substitution at the  $\alpha$ -position.

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