

# Solvent Effect on the Solvolysis of Phthalate Ester in Water-t Butanol Solvent- A Kinetic Study

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**Abstract :** The kinetic study of the solvent effect of alkali catalysed hydrolysis of dimethyl phthalate was studied in water-t-butanol media having varying concentration of t-butanol (from 20 to 80% v/v). The rate of the reaction was found depleting with gradual addition of the organic content (t-butanol) of the reaction were found to be enhanced simultaneously with the addition of more and more t-butanol in the reaction media. From the simultaneous enhancement in three thermodynamic parameters, it has been inferred that the sold reaction is enthalpy dominating and entropy controlled. From the plots of  $rH^*$  against  $rS^*$ , the iso-kinetic temperature of the reaction has been evaluated from the slope of the plot. The numerical value of its kinetic iso-kinetic temperature, which is greater than 300, it has been inferred that there is strong solvent-solute interaction in the reaction media in presence of t-butanol in it.

**Keyword:** Depleting, Activation Parameter, Solvent-solute Interaction, iso-kinetic Temperature, Specific Salvation, Stabilizer Operator.

## I. INTRODUCTION

Though the solvent effect on the rate and mechanism of the various types of the reaction has been reported<sup>1-4</sup>, but little attention has been paid towards the study of the solvent effect on the thermodynamic activation parameters and solvent-solute interaction, particularly for solvolysis of phthalate ester which seems to be important due to its mosquito and other insects repelling chemical properties. In order to highlight the above noted idea, it has been proposed to make a kinetic study of the solvent effect on the base catalysed hydrolysis of dimethyl phthalate in water-t-butanol media of various compositions.

## II. EXPERIMENTAL

The kinetics of base catalysed hydrolysis of dimethyl phthalate has been carried out in water-t-butanol media having different concentration of tertiary butanol varying from 20 to 80%(v/v) and at four different temperatures ranging from 20 to 40°C at regular interval of 5°C. The second order specific rate constant values of the reaction have been found decreasing with increase in t-butanol content in the reaction media and these have been mentioned in Table – 1.

The evaluated thermodynamic activation parameters have been tabulated in Table-II. The values of  $\Delta H^*$  and  $\Delta S^*$  at 30°C have been inserted in Table in order to evaluate the value of Iso-kinetic temperatures of the reaction.

## III. RESULTS AND DISCUSSION

### Solvent Effect on Thermodynamic Activation Parameters:

The thermodynamic activation parameters such as enthalpy of activation  $\Delta H^*$ , entropy of activation  $\Delta S^*$  and free energy of activation  $\Delta G^*$ , are the better indicators of the solvent effects exerted by the solvent on the solvolysis reaction. These thermodynamic activation parameters have been calculated with the help of Wynne- Jones and Eyring<sup>5</sup> equation and Absolute Rate Theory.

The values of all these three thermodynamic parameters, i.e.,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  at different mole % of the organic component of the reaction media have been synchronized in Table-II. On careful observation of the data, it is found that the  $\Delta G^*$  values increase from 82.23 kJ/mole to 85.45 kJ/mole with change of proportion of t-butanol from 20 to 80% (v/v) at 30°C. Though the enhancements not very large, however, it is not liable to be ignored, rather it is quite considerable.

The report of Yagil and Anbar indicated that OH ion of NaOH is hydrated with three molecules of water. In mixed aquo-organic co-solvent mixtures, organic component molecules are expected to contribute to the process of desolvation as they may be regarded as poor anion solvator in comparison to water. A similar variation in  $\Delta G^*$  values with increasing mole % of the organic co-solvent has also been reported previously by Cleave and Tommila and recently by Singh et. al. It is obvious the  $\Delta G^*$  value increases smoothly with increasing mole % t-butanol in the reaction media. This gradual and linear increase in  $\Delta G^*$  values with increase in mole % of the organic component in the reaction media is indicative of solvation or desolvation of reactants as explained by Absolute Reaction Rate Theory and also reported by Elsemony et. al. So far as variation in  $\Delta H^*$  and  $\Delta S^*$  are concerned, it is clear from the Table-II that both of them increase with increasing mole % of t-butanol in the reaction media. However, on perusal of the Table-II, it is interestingly observed that all the three thermodynamic parameters of the reaction namely  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  are found to increase simultaneously with increase in mole % of the organic component of the reaction media.

According to relation,

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

It can be easily concluded that simultaneous increase in  $\Delta G^*$  values with increase in  $\Delta H^*$  and  $\Delta S^*$  values is only possible when the extent of enhancement in  $\Delta H^*$  values is only possible when the extent of enhancement in  $\Delta H^*$  values is greater than that found in  $\Delta S^*$  values. The regular enhancement to the greater extent in  $\Delta H^*$  values in comparison to that of  $\Delta S^*$  values clearly indicates that base catalyzed hydrolysis of dimethyl phthalate in water-t-butanol media is enthalpy dominating and entropy controlled. Moreover, as found, the non linearity found in  $\Delta S^*$  curves with mole % of t-butanol gives information of the fact that specific solvation is taking place in water-t-butanol systems as already reported by Saville et. al. and it also indicates that the random distribution of the components are not acceptable. The similar non-linear variations in  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  values with increasing mole % of the organic co-solvent in the reaction media as shown in Figures-1, 2 and 3 respectively have also been reported by Tommila et. al. Singh and Jha and recently by Upadhyay & Singh.

### Iso-kinetic Relationship:

Barclay and Butler<sup>17</sup> have derived an iso-kinetic relationship between enthalpy of activation  $\Delta H^*$  and entropy of activation  $\Delta S^*$  as follows:

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

Where ' $\beta$ ' is a constant called iso-kinetic temperature and also known some times before as Leffler-Grunwald solvent stabilizer operator<sup>18</sup>. Leffler<sup>19</sup> has pointed out that plot of  $\Delta H^*$  against  $\Delta S^*$  results in a straight line and the slope of the line gives the value of iso-kinetic temperature ( $\beta$ ). He pointed out that many solvolysis reactions the values slope of the plots of  $\Delta H^*$  versus  $\Delta S^*$  come in between 300 and 400 and this foretells about the considerable interaction between solvent and solute of the reaction mixture.

In the present study also, plot of  $\Delta H^*$  versus  $\Delta S^*$  has been found linear (as shown in Figure-4) which is in conformity with Barclay- Butler relationship. The numerical value of the slope of the straight line is found to be 364.03. thus in the light of Leffler's guide lines, from the value of the slope which is far greater than 300, it can easily be concluded that there is appreciable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to strong interaction between solvent and solute

present in the reaction mixture (water-t-butanol media) in the similar way as reported by Lefler<sup>19</sup>. The structural changes with increasing proportion of the t-butanol in water-t-butanol media are responsible for the decrease in the specific rate constant values.

Recently Singh et.al. have reported the similar conclusions on solvent-solute interaction as that of ours.

**Table-I**

Specific rate constant values for alkali catalysed hydrolysis of dimethyl phthalate in water-t-butanol media  $k \times 10^2$  in  $(\text{dm})^3 \text{mole}^{-1} \text{min}^{-1}$

Temp in 0C	% of EG (v/v)						
	20%	30%	40%	50%	60%	70%	80%
200C	83.68	69.18	55.08	41.57	28.13	19.99	14.00
250C	153.63	140.63	118.63	87.74	66.83	45.81	31.12
300C	298.76	268.73	230.83	190.85	139.83	116.75	82.26
350C	580.53	540.85	430.32	378.76	282.65	225.63	175.63
400C	1124.60	1023.29	917.83	759.78	563.23	452.90	391.74

**Table-II**

Values of  $\Delta H^*$  and  $(\Delta S^*+100)$  at 30°C In water-t-butanol media

% of t-butanol (v/v)	Mole % of t-butanol	$\Delta H^*$ kj/mole	$\Delta S^*$ at 30°C j/k mole
20%	4.52	96.59	47.20
30%	7.51	101.01	60.47
40%	11.21	105.04	72.11
50%	15.13	107.83	79.49
60%	22.13	109.07	80.97
70%	30.66	113.13	92.47
80%	43.11	124.40	125.65

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**Table-III**Variation of log k values of the reaction with log [H<sub>2</sub>O] values in water-EtOH media

% of EtOH	% of water	Log [H <sub>2</sub> O]	3+log k value				
			20°C	25°C	30°C	35°C	40°C
30%	70%	1.5898	1.917	2.187	2.449	2.691	2.939
40%	60%	1.5220	1.834	2.115	2.388	2.643	2.049
50%	50%	1.4437	1.733	2.029	2.322	2.593	2.861
60%	40%	1.3160	1.611	1.922	2.230	2.518	2.806
70%	30%	1.2218	1.463	1.800	2.158	2.448	2.263
80%	20%	1.0458	1.192	1.574	1.951	2.304	2.661

**Table-IV**Values of slopes of the plots of log k versus log [H<sub>2</sub>O] in water-EtOH media.

Temperature in 0°C	Value of Slops
20°C	1.310
25°C	1.060
30°C	0.900
35°C	0.687
40°C	0.491

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