

A KINETIC STUDY OF CATALYSED SOLVOLYSIS OF MALONATE ESTER IN WATER-DIOXAN SOLVENT SYSTEMS.

RENU KUMARI¹ NAMRATA² RAHUL KUMAR³ AND R.T.SINGH⁴

1,2 and 3, -Research Scholars, Dept of Chemistry, V.K.S. University, Ara

4. Professor and Formerly HOD Chemistry and the Dean of the Faculty of Science, V.K.S. University, Ara

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ABSTRACT

Malonate ester contains active methylene group and is very useful; in Synthesis a large number of compounds, Such as barbiturates artificial flavourings, Vitamin B, and vitamin B6. It is also used as preservative for the up-to-date Societies.

In-order to Highlight-the Solvent effect on its activities, the kinetics of alkali Catalysed hydrolysis of diethyl malonate was studied in Water-Dioxan reaction media.

Out of the three thermodynamic activation parameters, namely ΔH^* , ΔG^* and ΔS^* , ΔH^* and ΔS^* values of the reaction were found to decrease simultaneously with increase in ΔG^* value and this shows that the dioxan behaves as an entropy controlling solvent.

The iso-kinetic temperature of the reaction is found to be 285, from which it is inferred that there is weak solvent-solute interaction in aquo-dioxan reaction media.

Introduction:

Although a lot of researches on the solvent effect have been carried out on the catalysed solvolysis of simple esters, but a little attention has been paid towards the study of acid or alkali catalysed hydrolysis of dibasic acid esters.

Therefore it has been proposed to study the alkali catalysed hydrolysis of diethyl malonate (dibasic ester) in aquo-dioxan media for highlighting the effect of dioxan on the activeness of methylene group present in the ester.

Experimental :

The kinetic of alkali catalysed hydrolysis of diethyl malonate was studied as usual^{1,2} at five different temperatures ranging from 20 to 40°C (at interval of 5°C) in aquo-dioxan media whose composition were varied from 10% to 50% (v/v) at interval of 10% in each case.

The reaction was found to obey second order kinetic equation and the evaluated values of specific rate constants of the reaction have been tabulated in Table-I.

Table- I

Specific rate constant values of Alkali catalysed hydrolysis of diethyl malonate in aquo-dioxan media
 $K_x \times 10^2$ in $\text{lit. mol}^{-1} \text{min}^{-1}$

Temp in °C	% of Dioxan (v/v)				
	10%	20%	30%	40%	50%
20 °C	49.1	42.9	37.2	34.3	32.2
25 °C	69.5	61.8	49.0	45.9	40.8
30 °C	111.9	87.5	78.3	63.7	56.6
35 °C	150.7	127.1	110.2	90.6	73.3
40 °C	205.1	178.2	149.6	116.7	97.5

From the slopes of the Arrhenius plots of $\log k$ versus $1/T$ (their values recorded in Table - II) the iso composition activation energy (E_c) values of the reaction for different concentration of dioxan were evaluated which are enlisted in Table-III.

Table - II

Variation of log k values with 1/T for alkali catalysed hydrolysis of diethyl malonate in aquo-Dioxan media.

Temperature	$10^3/T$	2 + log k values				
		10%	20%	30%	40%	50%
20	3.413	1.691	1.632	1.571	1.535	1.508
25	3.356	1.842	1.791	1.690	1.662	1.611
30	3.300	2.049	1.942	1.894	1.804	1.753
35	3.247	2.178	2.104	2.042	1.957	1.865
40	3.195	2.312	2.251	2.175	2.067	1.989

Similarly, from the slopes of Arrhenius Plots of log k_D values (log k_D obtained from the interpolation of plots of log k values verses D values of the reaction media as recorded in Table - IV and interpolated log K_D values at desired D values of the reaction media are inserted in Table - V) verses 1/T, the E_D values were evaluated and are placed in Table -VI. The thermodynamic activation parameters were evaluated by using Wynne-Jones and Eyring³ equation and are depicted in Table - VII.

Table - III

Evaluated values of Iso-composition Activation Energy (E_C or E_{exp}) for alkali catalysed hydrolysis of Diethyl malonate in aquo-Dioxan media

% of Dioxan	10%	20%	30%	40%	50%
E_C or E_{Exp} value in kJ/mol	58.22	55.61	54.96	48.45	42.76

Discussion on the Resultss:**Effect of solvent on the Activation energy (Iso-omposition) of the reaction:**

From the slopes of the Arrhenius plots of $\log k$ versus $1/T$, the iso-composition activation energy (E_C) of the reaction were evaluated and have been inserted in Table - IV.

Table - IV

$\log k_D$ values obtained from interpolation at different values of D for alkli catalysed hydrolysis of diethyl malonate in aquo-Dioxan media

Temp. °C	$10^3/T$	$2 + \log k_D$ values						
		34	40	46	52	58	64	70
20	3.413	1.494	1.525	1.556	1.590	1.621	1.654	1.686
25	3.356	1.598	1.643	1.689	1.734	1.779	1.825	1.870
30	3.300	1.732	1.792	1.853	1.914	1.975	2.036	2.098
35	3.247	1.901	1.957	2.014	2.070	2.127	2.185	2.241

From Table - IV, it is observed that the values of Iso-composition activation energy go on depleting from 58.22 kJ/mol to 42.76 kJ/mol with gradual addition of the organic content (dioxan) of the reaction media. The decrease in the values of Iso-composition activation energy may be caused by either of the following facts:

- (i) The initial state is desolvated and the transition state is solvated,
- (ii) The initial state is less solvated than the transition state, and
- (ii) The transition state is less desolvated than the initial state.

Table - V

**Iso-dielectric Activation Energy (E_D) values for alkali catalysed hydrolysis
of Diethyl malonate in aquo-Dioxan media.**

D values	D=34	D=40	D=46	D=52	D=58	D=64	D=70
E_D values in kJ/mol	52.19	54.56	56.05	58.21	60.40	62.12	64.07

Out of these three factors, the first one is expected to be operative in this case which gets support from the fact that the values of entropy of activation go on depleting with increasing the concentration of dioxan in the reaction media as recorded in Table - VII. This gives information of the fact that disorderness in the reaction media decreases. This conclusion is found in support of the earlier findings of Singh & Singh et al.⁴ and Rai & Singh et al.⁵. Recently Akanksha & Singh et al.⁶, Kumar & Singh et al.⁷ and R. T. Singh⁸ have also interpreted similar conclusions for depletion in Iso-composition activation energy of solvolysis reactions.

Effect of aquo-dioxan reaction media on the Iso-dielectric activation energy (E_D) of the Reaction :

Plots of $\log k$ versus D and plots of $\log K_D$ versus $1/T$. On perusal of the data of Table -VI, it is apparant that E_D values of the reaction are found to increase with D values of the reaction media. The E_D values is 52.19 kJ/mol at dielectric constant value $D = 34$ and enhances to 64.07 kJ/mol at $D = 70$. As dielectric constant value of aquo-dioxan media inceases with gradual addition of dioxan in the reaction media as shown in Table - IV, so in another way, it may be concluded that like Iso-composition activation energy (E_C), the Iso-

dielectric activation energy (E_D) of the alkali catalysed hydrolysis of diethyl malonate are also decreasing with gradual addition of (vol%) of the organic cosolvent (dioxan) in the reaction media. From above interpretation about E_C and E_D , it may be inferred that they (E_C or E_D) are complimentary to each other. Similar observation and inferences regarding solvent effect on E_D values of the reaction have also been reported earlier by Priyanka & Singh et al.⁹ and recently by Choubey & Singh et al.¹⁰

Table -VI

Variation of log k with the Dielectric constant 'D' of aquo-Dioxan for Alkali catalysed hydrolysis of Diethyl malonate in aquo-Dioxan media at different temperatures.

% of Dioxan (v/v)	2 + log k values							
	20°C		25°C		30°		35°C	
	D	2 + log k	D	2 + log k	D	2 + log k	D	2+log k
10	68.3	1.691	66.4	1.842	65.3	2.049	63.3	2.178
20	59.8	1.632	58.7	1.791	57.1	1.942	48.5	2.104
30	52.6	1.571	51.3	1.690	49.9	1.894	40.0	2.042
40	43.6	1.535	42.3	1.662	41.1	1.804	40.0	1.957
50	34.7	1.508	33.7	1.611	32.7	1.753	31.6	1.865

Effect of solvent on Thermodynamic Activation Parameters of the Reaction:

The consolidated values of ΔH^* , ΔG^* and ΔS^* have been synchronised in Table - VII and their variation with mol % of dioxan. From Table - VII, which includes the values of the three thermodynamic activation parameters i.e ΔH^* , ΔS^* and ΔG^* , it is observed that values of free energy of activation ΔG^* enhance from 84.29 kJ/mol to 86.01 kJ/mol with gradual addition of dioxan from 10 to 50% (v/v) in the reaction media at 30°C. Though the enhancement in ΔG^* values is not very high, but, is very much liable to be taken into

consideration. Similar variations in ΔG^* values have also been reported earlier by Tommila¹¹ and Dubey & Singh et al.¹². From the plots of ΔG^* values with mol % of dioxan a smooth curve is obtained which is indicative of solvation or desolvation of reactants as explained by Elsemongy et al.¹³ While variation in ΔH^* and ΔS^* are concerned, it is clear from Table VII, that both of them decrease with increasing mol % of dioxan in the reaction media. However, from Table- VII, it is interesting to observe that out of all the three thermodynamic activation parameters of the reaction, namely ΔH^* , ΔG^* and ΔS^* , there is depletion in ΔH^* and ΔS^* values with simultaneous increase in ΔG^* with gradual addition of dioxan in the reaction media.

According to the relation

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

it can easily be concluded that the simultaneous enhancement in ΔG^* values with decrease in ΔH^* and ΔS^* values is only possible when the extent of depletion in ΔS^* is greater than that of ΔH^* . The regular depletion to the greater extent in ΔS^* values in comparison to the ΔH^* values clearly indicates that the alkali catalysed solvolysis of diethyl malonate in aquo-dioxan media is enthalpy domination and the organic co-solvent dioxan plays the role of entropy controlling solvent.

Moreover, the non-linear variation (depletion) in ΔH^* and ΔS^* values with gradual addition of dioxan in the reaction media gives information of the fact that the specific solvation is taking place in aquo-dioxan solvent system which is in accordance with the observation of Tommila et al.¹¹. Similar findings regarding effect of solvent on the thermodynamic activation parameters have also been reported earlier by Singh & Singh et al.¹⁴, Singh & Priyanka et al.¹⁵ and recently by Shurma & Singh et al.¹⁶.

Evaluation of Iso-Kinetic temperature of the Reaction and Solvent solute Interaction in aquo-dioxan media:

With the help of Iso-kinetic relationship developed by Barclay and Butler¹⁷, the value of the Iso-kinetic temperature was evaluated.

The Barclay and Butler equation is:

$$\delta_m (\Delta H^*) = \beta \delta_m (\Delta S^*)$$

It is a relationship between enthalpy and entropy of activation and ' β ' is called Iso-kinetic temperature which is also called Leffler-Grunwald¹⁸ solvent stabilizer operator.

In the light of the above mentioned relationship, the value of Iso-kinetic temperature of the reaction was evaluated from the slope of the plots of ΔH^* against ΔS^* from their values as recorded in Table - VII and comes to 285.0 In the light of Leffler's¹⁹ guidelines, it is concluded from the numerical value of the slope (which is less than 300), that there is considerable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to weak but appreciable interaction between solvent and solute present in the reaction media (aquo-dioxan media).

Table – VII

Thermodynamic Activation parameters for Alkali catalysed hydrolysis of Diethyl malonate in aquo-Dioxan Media.

ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/K/mol

% of Dioxan (v/v)	ΔH^* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
		ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
10%	55.90	83.44	93.99	84.04	94.43	84.29	93.71	84.96	94.37	85.58	94.83
20%	53.83	83.77	102.17	84.33	102.34	84.91	102.58	85.40	102.49	85.95	102.61
30%	52.07	84.11	109.33	84.91	110.17	85.19	109.30	85.76	109.38	86.40	109.67
40%	45.93	84.31	131.00	85.06	131.33	85.72	131.31	86.27	130.97	87.05	131.37
50%	40.05	84.46	151.57	85.36	152.03	86.01	151.67	86.81	151.18	87.52	151.64

Similar findings and inferences regarding solvent-solute interaction have also been recorded earlier by Singh & Singh et al.²⁰, Dubey & Singh et al.²¹ and recently by Sinha & Singh et al.²² Sushma & Singh et al.²³. and Sushma- abhay and Singh et al.²⁴.

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