

EFFECT OF 1:4 DIOXAN ON THE ACTIVATION ENERGIES, AND MECHANISM OF THE CATALYSED SOLVOLYSIS OF CAPRYLATES

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ABSTRACT

The rate and the thermodynamic parameters of solvolysis of Methyl caprylate have been found to be affected by the gradual addition of the organic cosolvent (Dioxan) in the reaction media. The changes observed in the values of thermodynamic activation parameters such as ΔH^* , ΔS^* and ΔG^* have been found to be better indicators of the solvent effect exerted by the solvent on the solvolysis reactions.

Introduction:

With view to highlight solvent effect of dioxan on the carried biochemical uses of caprylic acid, the alkali catalysed hydrolysis of Methyl caprylate was carried out in aquo-Dioxan solvent systems of different composition varying from 20 to 80% (v/v) of the organic cosolvent (Dioxan) at five different temperatures ranging from 20°C to 40°C. The depletion in the values of specific rate constants along with decrease and increase in the iso-composition and iso-dielectric activation energies (Iso-composition) with increase in concentration of Dioxan in the reaction media has been explained in the light of solvation and desolvation of initial and transition state respectively of the reaction. Solvent-solute interaction was also evaluated quantitatively by using Barclay-Butler¹ rule.

Experimental

The kinetics of alkali catalysed hydrolysis of Methyl caprylate in aquo-Dioxan media was studied following the earlier reported processes^{2,3}. The reaction was found to obey second order kinetic equation and the evaluated values of specific rate constants of the reaction are recorded in Table-I. From the slopes of the Arrhenius plots of $\log k$ versus $1/T$ from their values enlisted in Table-II, the Iso-composition activation energy(E_C) values were evaluated which have been placed in Table -III.

Similarly, from the slopes of the Arrhenius plots of $\log k_D$ values ($\log k_D$ obtained from the interpolation of plots of $\log k$ values verses at desired 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) versus $1/T$, the E_D values were evaluated and are placed in Table -VI. The thermodynamic activation parameters were evaluated by using Wunne-Jones and Eyring⁴ equation and are depicted in Table -VII.

Discussion on the Results:

Effect of Solvent on the Activation energy(Iso-composition) 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 -III.

From Table - III. it is observed that the values of Iso-composition activation energy go on depleting from 91.99 kJ/mol to 67.03 kJ/mole with gradual addition of the organic constant (dioxan)

Table - 1

Specific rate constant values of Alkali catalysed hydrolysis of Methyl caprylate in water-Dioxan media

$k \times 10^3 \text{ in (dm)}^3 \text{ mole}^{-1} \text{ min}^{-1}$

Temp in °C	% of DMF (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	77.55	70.62	65.86	62.78	58.63	53.73	47.25
25°C	144.61	136.30	117.52	109.09	100.76	88.88	77.20
30°C	279.64	253.69	225.22	202.35	174.42	154.74	125.55
35°C	474.46	416.77	362.91	316.37	274.03	227.09	180.80
40°C	851.92	746.62	616.74	536.91	449.06	363.50	279.38

Table - II

Variation of log k values of the reaction at different temperatures with mol% of DMF in water-DMF media.

Temp. °C	10^3 T	3 + log k values at different % Dioxan(v/v)						
		20%	30%	40%	50%	60%	70%	80%
20°C	3.413	1.8896	1.8489	1.8186	1.7978	1.7681	1.7302	1.6744
25°C	3.356	2.1602	2.1345	2.0701	2.0378	2.0033	1.9488	1.8876
30°C	3.300	2.4466	2.4043	2.3526	2.3061	2.2416	2.1896	2.0988
35°C	3.247	2.6762	2.6198	2.5598	2.5002	2.4378	2.3562	2.2572
40°C	3.195	2.9304	2.8731	2.7901	2.7299	2.6523	2.5605	2.4462

The decrease in the values of iso-composition activation energy may be caused by either of the following factors:

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

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 has been supported by the earlier findings of Singh & Singh et al.⁵, Rai & Singh et al.⁶, Akanksha & Singh et al.⁷ and Kumar & Singh et al.⁸. Recently, R. T. Singh⁹ and N. Kumar¹⁰ 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 :

On perusal of the data of Table- VI, it is apparent that E_D values of the reaction are found to increase with D values of the reaction media. The E_D values is 72.01 kJ/mol at dielectric constant value $D = 10$ and enhances to 95.85 kJ/mol at $D = 60$. As dielectric constant value of aquo-Dioxan media decreases 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

Table - III

Evaluated values of Iso-composition Activation Energy (E_c or E_{exp})
of the reaction in water-Dioxan media.

% of Dioxan	20%	30%	40%	50%	60%	70%	80%
E_c value in kJ/mol	91.99	89.50	85.70	83.48	77.41	72.60	67.03

the alkali catalysed hydrolysis of Methyl caprylate are also decreasing with gradual addition of (vol%) of the organic cosolvent (Dioxan) in the reaction media. From above interpretations about E_C and E_D , it may be inferred that they (E_C and E_D) are complimentary to each other. Similar observations and inferences regarding solvent effect on E_D values of the reaction have also been reported earlier by Priyanka & Singh et al.¹¹ and Kumari & Singh et al.¹² and recently by Singh⁹ and Kumar¹⁰.

Effect of Solvent on Thermodynamic Activation Parameters of the Reaction:

The consolidated values of ΔH^* , ΔS^* and ΔG^* , it is obvious that values of free energy of activation ΔG^* enhance from 87.78 kJ/mol to 89.80 kJ/mol with gradual addition of Dioxan from 20 to 80% (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 Tommila¹³ and Dubey & Singh et al.¹⁴. 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.¹⁵ While variations in ΔH^* and ΔS^* , 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 ΔG^* , ΔH^* and ΔS^* , there is depletion in ΔH^* and ΔS^* values with simultaneous increase in ΔG^* , ΔH^*

and ΔS^* , there is depletion in ΔH^* and ΔS^* values with simultaneous invresase in ΔG^* with gradual addition of Dioxan in the reaction media.

According to 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^* values is greater

Table -IV

Variationof log k values with D (Dielectric constant) 3+log k values of water-Dioxan media at different temperatures.

% of Dioxan (v/v)	Mol % of Dioxan	20°C		25°C		30°C		35°C		40°C	
		D	3+log k	D	3+log k	D	3+log k	D	3+log k	D	3+log k
20%	5.02	59.80	1.8896	58.70	2.1602	57.10	2.4466	55.81	2.6762	54.61	2.9304
30%	8.31	52.60	1.8489	51.30	2.1345	49.90	2.4043	48.50	2.6198	47.31	2.8731
40%	12.36	43.61	1.8186	42.30	2.0701	41.10	2.3526	40.00	2.5598	38.90	2.7901
50%	17.46	34.70	1.7987	33.70	2.0378	32.71	2.3061	31.60	2.5002	30.50	2.7299
60%	24.08	25.90	1.7681	25.10	2.0033	24.20	2.2416	23.40	2.4378	22.60	2.6523
70%	38.04	17.20	1.7302	16.30	1.9488	15.50	2.1896	14.80	2.3562	14.20	2.5605
80%	45.83	10.10	1.6744	09.65	1.8876	09.10	2.0988	08.60	2.2572	08.10	2.4462

Table -V

**Variation of Interpolated log K_D values at different desired D values
of water-Dioxan media with temperature**

Temp. °C	10^3 T	D = 10	D = 20	D = 30	D = 40	D = 50	D = 60
20°C	3.413	1.6878	1.7261	1.7643	1.8063	1.8486	1.8793
25°C	3.356	1.9062	1.9589	2.0114	2.0626	2.1176	2.1705
30°C	3.300	2.1502	2.2152	2.2791	2.3424	2.4052	2.4726
35°C	2.247	2.3151	2.3942	2.4725	2.5539	2.6332	2.7148
40°	3.195	2.5199	2.6102	2.7073	207952	2.8892	2.9812

than that of ΔH^* . The regular depletion on the greater extent in ΔS^* values in comparison to the ΔH^* values clearly indicates that the alkali catalysed solvolysis of Methyl caprylate in aquo- Dioxan media is enthalpy dominating 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 Dioan in the reactionmedia, gives information of the fact that the specific solvation is taking place in aquo-Dioxan solvent systems which is in accordance with the observation of Tommila et al.¹³ and Singh & Jha et al.¹⁶. Similar

Table - VI

D values	D = 10	D = 20	D = 30	D = 40	D = 50	D = 60

E_D values in kJ/mol	72.01	76.95	82.54	86.74	91.31	95.85
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Evaluated values of Iso-Dielectric Activation Energy (E_D) of the reaction at different desired 'D' valus of the water-Dioxan media.

findings regarding effect of solvent on the thermodynamic activation parameters have also been reported recently by Singh & Singh et al.¹⁷ and Choubey & Singh et al.¹⁸.

Evaluation of Iso-kinetic temperature of the Reaction and Solvent-solute Interaction in aquo-Dioxan reaction media :

With the help of iso-kinetic relationship developed by Barclay and Butler¹, 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-Grunwald¹⁹ 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 $281.56 \approx 282.0$ In the light of Leffler's²⁰ 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).

Similar conclusion and inferences regarding solvent-solute interaction have also been recorded earlier by Dubey & Singh et al.²¹ and Singh & Singh et al.²² and recently by Sinha & Singh et al.²³

Table - VII

Consolidated Values of Thermodynamic Activation parameters (ΔH^* , ΔG^* and ΔS^*) of the reaction in water-Dioxan system at different temperatures.

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

% of Dioxan (v/v)	Mole % of Dioxan	ΔH^* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
20%	5.02	89.16	87.93	4.21	87.93	4.15	87.78	4.55	87.92	4.04	87.87	4.15
30%	8.31	86.52	88.16	-5.59	88.08	-5.22	88.03	-4.98	88.25	-5.67	88.21	-5.40
40%	12.36	82.39	88.33	-20.25	88.44	-20.30	88.33	-19.59	88.61	-20.17	88.71	-20.17
50%	17.46	79.23	88.45	-31.45	88.63	-31.54	88.60	-30.92	88.96	-31.59	89.07	-31.43
60%	24.08	75.47	88.61	-44.84	88.82	-44.80	88.97	-44.56	89.33	-44.98	89.53	-44.92
70%	38.04	70.56	88.83	-62.33	89.14	-62.33	89.28	-61.76	89.81	-62.49	90.08	-62.37
80%	45.83	63.48	89.14	-87.57	89.48	-86.05	89.80	-86.87	90.39	-87.38	90.77	-87.18

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