JOURNAL OF ULTRA CHEMISTRY

Studies on the effect of Dielectric constants of Aquo-DMF Solvent- System of the Solvolysis Products of Nicotinates

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http://dx.doi.org/10.22147/juc/160504

Abstract

From the eenhancement observed in ΔG^* values with simultaneous decrease in the values of ΔH and ΔS^* of the reaction, it is concluded that the organic co-solvent dimethyl formamide (DMF) acts as entropy controller and enthalpy stimulator solvent for alkali catalysed solvolysis of Methyl nicotinate.

Form the evaluated values of water molecules associated with the activated complex of the reaction which are found to increase with increase in the temperature of the reaction, it is inferred that the bimolecular mechanistic path is changed to unimolecular in presence of the organic component (DMF) of the reaction media. The numerical value of Iso-Kinetic temperature of the reaction which comes to be nearly 287.5 (below 300) indicates that there is weak but considerable solvent-solute interaction in the aquo-DMF solvent system.

Key words : Dielectric Constants Solvent- Systeme, Solvolysis, Mechanism, Solvation number, unimolecular, Biomolecular, Transition State.

Introduction

Though a large number of kineticists[1-2] of the kinetic have reported the effect of solvents on the rates, mechanism and the thermodynamic properties of hydrolysis of simple esters, but, a little attention has been paid towards the studies of solvent effect of dipolar aprotic solvent-Dimethyl formamide (DMF) on the rate, mechanism and thermodynamic activation parameters of the reaction and solvent-solute interaction for alkali catalysed solvolysis of nicotinate esters which has medicinal potential and industrial uses for being used as insecticides which enhance yield of agricultural products.

Experimental & Calculation

The kinetics of alkali catalysed hydrolysis of Methyl nicotinate was carried out separately in the different aquo-organic co-solvent media (aquo-DMF) prepared by adding different volumes of DMF (20 to 80% v/v). The strength of the solution was kept 0.1 M With respect of NaOH and 0.05 M with respect to the ester. The reaction was found to follow the second order kinetic equation and the evaluated values of specific rate constants have been recorded in Table 1. For studying the effect of changes of concentration of organic component (DMF), the variation of log k values of the reaction with mol% of acetone in the reaction media has been enlisted in Table 2. Using Arrhenius equation, the iso-composition and iso-dielectric activation energies values of the reaction were evaluated and are recorded respectively in Table 3 & 4. The thermodynamic activation parameters such as ΔH^*, ΔG and ΔS^* have been evaluated using Wynne-Jones and Eyring[3] equation and their consolidated values have been shown in Table 5.

For studying the mechanism of the reaction, the number of water molecules associated with the transition state of the reaction in reaction media at different temperatures have been evaluated by the use of Robertson equation[4] and are depicted in Table 6.

Table 1

Specific rate constant values of Alkali catalysed hydrolysis of Methyl nicotinate in water-DMF media

$k \times 10^2$ in $(dm)^3 \, mole^{-1} \, min^{-1}$

Tempin °C	% of DMF (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	40.82	37.72	34.86	32.82	30.70	27.87	25.12
25°C	86.38	77.37	68.85	62.13	55.26	47.91	41.51
30°C	184.29	157.62	136.36	118.09	99.68	83.14	67.78
35°C	371.19	306.97	257.22	213.99	174.22	138.23	108.02
40°C	741.65	605.48	488.43	391.20	302.41	234.15	170.70

Table 2

Variation of log k values of the reaction at different temperetures

with mol% of DMF in water-DMF media.

% of DMF (v/v)	Mol % of DMF	2 + log k values				
		20°C	25°C	30°C	35°C	40°C
20%	5.53	1.1609	1.9364	2.2655	2.5696	2.8702
30%	9.12	1.5766	1.8886	2.1976	2.4871	2.7821
40%	13.50	1.5423	1.8379	2.1347	2.4103	2.6888
50%	18.96	1.5161	1.7933	2.0722	2.3304	2.5924
60%	25.99	1.4871	1.7424	1.9986	2.2411	2.4806
70%	35.27	1.4451	1.6802	1.9198	2.1406	2.3695
80%	48.29	1.4000	1.6182	1.8311	2.0335	2.2314

Table 3.

Evaluated values of Iso-composition Activation Energy (E_c or E_{exp})

of the reaction in water-DMF media

% of DMF (v/v)	20%	30%	40%	50%	60%	70%	80%
E_c value in kJ/mol	111.04	106.52	101.73	96.26	88.72	81.97	73.61

Table 4

Evaluated values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction at Different

Desired "D" values of the water-DMF media

D values E_c value in kJ/mol	D = 50	D = 55	D = 60	D = 65	D = 70	D = 75
	78.91	88.52	96.74	107.00	115.36	124.39

Table 5

Consolidated Values of Enthalpy of activatio (ΔH^*), Free energy of activation (ΔG^*) and Entropy of

activation(ΔS^*)of the reaction at different mol % of DMF in water-DMF media

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

% of DMF (v/v)	Mole % of DMF	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%	5.53	107.73	83.88	81.38	83.50	81.31	83.03	81.50	82.65	81.42	82.23	81.45
30%	9.12	104.19	84.08	68.66	83.77	68.52	83.43	68.54	83.14	68.36	82.76	68.47
40%	13.50	98.60	84.27	48.91	84.06	48.78	83.75	49.00	83.59	48.73	83.32	48.81
50%	18.96	92.22	84.42	26.65	84.32	26.54	84.15	26.63	84.06	26.49	83.90	26.60
60%	25.98	86.39	84.58	6.17	84.61	5.98	84.58	5.96	84.59	5.84	84.57	5.81
70%	35.27	79.79	84.81	-17.16	84.96	-17.36	85.04	-17.33	85.18	-17.52	85.24	-17.41
80%	48.29	71.08	85.07	-47.73	85.32	-47.76	85.55	-47.76	85.81	-47.83	86.06	-47.86

Table 6

Values of the slopes of the plots of log k versus log [H_2O] values at different temperatures

Temperature in °C	Slope - IBefore log [H_2O] value 1.398	Slope - IIAfter log[H_2O] value1.398
20°C	0.369	0.453
25°C	0.413	0.752
30°C	0.558	1.072
35°C	0.676	1.177
40°C	0.816	1.447

Results and Discussion

Effect of Solvent on the Specific Rate Constants of the Reaction :

In order to highlight the effect of the solvent on the specific rate constant values of the reaction, the log k values were plotted against the mole % of the organic co-solvent (their values from Table 2) and were found to follow decreasing trends. However, the depletion found in the rate with increasing mole % of the organic co-solvent at all the temperatures follow smooth path following two intersection straight lines at about 21.00 mol % of DMF having different numerical values of the slope (of similar nature) before and after the point of intersection (at about 21.00 mol % DMF in the reaction, the degree of depletion in the rate constants of the reaction becomes slower or shallow.

Howerer, the possible rate depleting factors in the rate can be listed as follows:
(i)   decrease in the bulk dielectric constant value of the medium.
(ii) decrease in the polarity of the reaction media on adding less polar DMF to it.

The above noted two depleting factors are quite in operation and this is quite in agreement with the theory of Hughes and Ingold[5] that the rate ought to decrease with decreasing dielectric constant of the reaction media.

Such decrease in rate constant with increasing proportion of the organic co-solvent like DMF have also been reported earlier by Anantkrishnan et al.[6] Essemongy et al[7] and recently also by Akanksha & Singh *et al.*[8] and Achari & Singh *et al*[9]. However, the decrease observed in the specific rate constant values with different numerical values of slopes may be attributed partly due to the dielectric effects of the reaction media and partly due to solvation changes taking place in it (aquo-DMF) reaction media.

Effect of Solvent on the Iso-composition Activation Energy (E_C) of the Reaction :

On perusal of the data mentioned in Table 3,

we observe that the value of Iso-composition activation energy of the reaction go on decreasing from 111.04 kJ/mol to 73.61 kJ/mol with increasing concentration of DMF from 20 to 80% (v/v), in the reaction media. The depletion E_C values of the reaction in water-acetone media may be due to either of the following three causes:
(i)   The transition state is solvated and the initial state is desolvated,
(ii)   The transition state is more solvated than the initial state, and
(iii) The transition state is less desolvated than the initial state.

Among these three factors, the first factor seems to be operative in this case as from the values of thermodynamic activation parameters of the recation in Table 5, both ΔH^* and ΔS^* values of the reaction are found to decrease with increasing proportion of DMF in the reaction media (ΔH^* values decreases from 107.18 kJ/mol to 71.08 kJ/mol and ΔS^* values decreases from 81.50 J/K/mol to -47.76 J/K/mol at 30°C).

Our such findings and their interpretations have been found in accordance with the earlier reports of Singh & Perween *et al.*[10] and also with the recent reports of Sharma & Singh *et al.*[11]

Solvent Effect on the Iso-dielectric energy (E_D) of the reaction:

From the values recorded in Table 4, it appears that E_D values of the reaction go on increasing with increasing dielectric constant values of the aquo-DMF reaction media. The E_D value is 78.91 kJ/mol at D value 50 and increases to 124.39 kJ/mol at D value 75. The enhancement in the E_D values with increase in D values of the reaction media is in accordance with depletion in E_C or E_{exp} values of the reaction with increasing mol % of DMF in the reaction media. These findings and conclusions have been found in support of the earlier reports of Wolford[12] and also with the recently reported findings by Haider & Singh *et al.*[13]

Solvent Effect on Thermodynamic Activation Parameters of the Reaction :

From Table 5, on perusal of the values of thermodynamic activation parameters, namely ΔG^*, ΔH^* and ΔS^*, it is observed that ΔG^* values (free energy of activation) of the reaction increases with simultaneous decrease in its ΔH^* and ΔS^* values. At 30°C, ΔG^* values have been observed increasing from 83.03 k cal/mol to 85.55 k cal/mol with increasing concentration of DMF from 20 to 80% (v/v) in the reaction media. Though this enhancement is not very large, however, it is quite considerable and acceptable too. In order to highlight the effect of changing concentration of the organic content (acetone) in the reaction media, ΔH^*, ΔG^* and ΔS^* values were plotted against the changing mol % of DMF in the reaction.

From the plots of ΔG^* values against mol % of DMF. it is found that ΔG^* values go on increasing non-linearly with gradual addition of acetone in the reaction media. This finding is indicative of desolvation of reactants as explained by Elsemongy *et al.*[14]

So far as the variation in ΔH^* and ΔS^* are concerned on observing their values from Table 5 and their plots against mol % of DMF. it is interestingly found that both of them decrease linearly and non-linearly respectively with gradual addition of DMF in the reaction media.

From the thermodynamic relation:
$$\Delta G^* = \Delta H^* - T\Delta S^*$$
it can be easily concluded that increase in ΔG^* values witth simultaneous decrease in both of ΔH^* and ΔS^* values is only possible when ΔS^* values decreases more than ΔH^* value. From such findings, it is inferred that in presence of acetone in the reaction media, the alkali catalysed hydrolysis of Methyl nicotinate becomes entropy controlled and enthalpy stimulate reaction. moreover, linear variation in ΔH^* and non-linear variation in ΔS^* values with increasing mol % of DMF, gives information of the support of the recent observation and inferences of Dheeraj & Singh *et al.*[16]. fact that specific solvation is taking place in water-DMF solvent systems similar to that as reported in the past by Savilly *et al.*[15] However, such interpretation have also been found in

Solvent Effect on Iso-Kinetic Temperature and Solvent-Solute Interaction in the Reaction Media:

The value of the iso-kinetic temperature of the reaction was ecaluated by using Barcley-Bulter[17] relationship which is expressed as
$$\delta m (\Delta H^*) = \beta \, \delta m (\Delta S^*)$$
It is a straight line equation representing the relationship between enthalpy and entropy of activation values of the reaction. 'β' is known as iso-kinetic temperature. From the values of ΔH^* and ΔS^* values available in Table 5, the plots of ΔH^* versus ΔS^* at 30°C. From the slope of the straight line of the plots, the values of the kinetic temperature was evaluated to be 287.54 (below 300). Thus, in the light of Lefller's guidelines[18], from the numerical values of the iso-kinetic temperature (which is below 300), it can safely be concluded that there is appreciable change in the structure of the reactant or in the solvent or in both the reactant and solvent due to weak but considerable interaction between solvent and solute present in the reaction media (aquo-DMF) in the similar way as reported earlier by Dubey & Singh *et al.*[19] and recently by Sushma & Singh *et al.*[20].

Conclusion

Due to weak but considerable interction in aquo-DMF reaction media the solvent DMF is acceprable solvent for nicotinates and it will act effectively as in secticide in presence of DMF.

References

1. Elsemongy, M. M. Abu Elamayan, M. S. and Moussa, M.N.H., Z. Physik Chem. (Neue Folge), 95, 215 (1975).
2. Singh, Lallan, Gupta, A.K., Singh, R.T., Verma, D.K. and Jha, R.C: React. Kinet. Catal Lett. 24, No (1-2), 161-165, (1984).
3. Wynne Jones W.F.K. and Eyring, H., *J. Chem. Phys., 3,* 492, (1935)
4. Robertson, R. E., Prog. Phy. Org., Chem. 4, 213, (1967).
5. Hughes, E. D. and Ingold, C.K., J. Chem. Soc.,

244, 255, (1935).

6. Anantkrishnan, V. and Radhakrishnamurthy, P.S., *Indian J. Chem., 3,* 336, (1965).

7. Elsemongy, M. M. Abu Elamayam, M.S. and Moussa, M.N.H., Z.Physik Chem. (Neue Folge), *94,* 215 (1975).

8. Akanksha, Kumari, R., Kumar, R. and Singh, R.T., *ARJ Phys. Sci., 17,* No. (1-2),

9. Achari R.S, Archana K and Singh RT., NIRJ Sci *22,* 67-77, (2016)(Dec)

10. Singh, R.T., Singh, A., Kumari, V. and Perween, M., ARJ Phys. Sci., 15, No.(1-2), 151-161, (2012).

11. Sharma S.P., Kumari S. Gautam S. and Singh R.T. NIRJ Sci *23,* 91-104, 2017(March)

12. Wolford, R.K., *J. Phys. Chem., 64,* 3392, (1964).

13. Haider R., Tauheed S. and Singh R.T., NIRJ *Sci 24,* 85-100, 2017(Sept)

14. Elsemongy, M. M. Abu Elamayan, M. S. and Moussa, M.N.H., Z. Physik Chem.(Neue Folge),

15. Saville, B.J. and Husdan, R.F., *J. Chem. Soc.,* 4114, (1955).

16. Dheeraj K., K. Vishal, K. Ragini and Singh R.T., *NIRJ Sci. 25,* 85-95, 2017(Dec)

17. Barclay, I.A. and Butler, J.A.V., Trans Faraday Soc., 34, 1445, (1938).

18. Leffler, J.E., *J. Org. Chem., 20,* 1201, (1955).

19. Dubey, R.B., Gautam, S., Singh, S.M. and Singh, U.C., ARJ Phys. Sci., 15, No.129-139 (2012).

20. Sushma, Rauram R.K. and Singh R.T., IJESM *7,* No(2), 147-162, 2018(Feb).

21. Robertson, R.E., Hippolitile, R.L. and Scott, J.M.W., *Canad. J. Chem. Soc., 37,* 303, (1959).

22. Monalisa, Singh, R.N., Sudhansu, N.S. and Singh, R.T., NIRJ Sci. *12,* 89-99, (2013).

23. Sushma K., Abhay A., Singh Arya N. and Singh R.T., JICS, 10 No (5) 794- 813, (2020).

84, 295, (1975).