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Solvent Interactions and Solvation Models in the Oxidation of Benzyl Alcohol by Quinolinium Dichromate

P. MANIKYAMBA
Department of Chemistry, Kakatiya University
Warangal-506 009, India

The kinetics of oxidation of benzyl alcohol by quinolinium dichromate has been studied in different pure protic and aprotic solvents. The rate data is correlated with different solvation parameters using linear multiple regression analysis. From the regression coefficients, information on the solvent-solute interactions is obtained and the solvation models are proposed.

Key Words: Solvation Model, Solvent Interactions, Oxidation, Benzyl alcohol, Kinetics.

INTRODUCTION

Although many advances have been achieved in the field of kinetics, the influence of solvent on chemical reactivity is still not understood completely due to lack of general theories. A solvent can influence the rate of any reaction by solvating the reactants and intermediates. Though a solvent is characterized by dielectric constant (ε), correlation of rate with this single parameter does not always give a complete picture of the nature of solvation of reactants and the intermediates. The solvent polarity has to be measured in terms of overall solvating ability of the solvent due to its properties like electrophilicity (E), nucleophilicity (B), hydrogen bond donor ability (α), hydrogen bond acceptor ability (β), polarisability (P) etc. Hence the effect of a solvent on a reaction rate has to be quantitatively expressed by a multiparametric equation[1],

$$\log k = \log k_0 + aA + bB + cC + \dots \qquad (1)$$

where k is the rate constant of the reaction in any solvent and k_0 is the rate constant in a reference solvent which doesn't solvate the reagent at all. The regression coefficients a, b, c etc. describe the susceptibility of k to the respective solvation parameters A, B, C, ... of the solvent. In our earlier studies[2–4] we applied such equations to the solvent effects in different nucleophilic substitution reactions. We have extended such study to the oxidation reaction also. We now report our results of solvent effects on the oxidation of benzyl alcohol by quinolinium dichromate.

EXPERIMENTAL

The substrate benzyl alcohol and the solvents dimethyl formamide, dimethyl sulphoxide, acetone, acetonitrile, benzonitrile and ethyl acetate were of E. Merck make. Formamide, methanol, ethanol, *n*-propanol, *t*-butanol, acetic acid, chloroform were Qualigens ExcelaR samples. The purity of these samples was checked and the solvents were distilled wherever necessary by following literature methods. Water was distilled twice and used. Quinolinium dichromate (QDC) was prepared following the procedure described in the literature[5]. Stock solutions of benzyl alcohol and oxidants of appropriate concentrations were prepared in pure solvents by dissolving the known volume and weighed quantity of the substrate and oxidant in different solvents. The solutions of the reactants were thermally equilibrated and mixed. The reactions were conducted at 30°C with 0.5 mol dm^{-3} benzyl alcohol and 1.00×10^{-3} mol dm^{-3} QDC in 100% solvent. The course of the reaction was followed by estimating the unreacted oxidant iodometrically at different time intervals. The plot of log $[QDC]_t$ against time gave linear plot with negative slope from which the pseudo first order rate constant k was calculated. These k values were reproducible within ±5% error.

These k values determined at different [QDC] in 30% (v/v) aqueous acetic acid medium were constant indicating that the reaction is first order in QDC[6]. Further, these pseudo first order rate constants, k, determined at different concentrations of benzyl alcohol were proportional to [BzOH] suggesting that the oxidation process is first order with respect to [BzOH] also. The oxidation product was identified to be benzaldehyde by preparing 2,4-dinitrophenyl hydrazone derivative and comparing its melting point with the literature value[6]. Similar results were obtained in the present study also when the reactions are conducted in 100% solvents.

RESULTS AND DISCUSSION

The reaction has been studied in fifteen different protic and dipolar aprotic solvents with a range of 60 units of dielectric constant. The pseudo first order rate constants k determined are presented in Table-1. When log k was correlated with any one of the solvent parameters discussed above, no meaningful relation is obtained. Some of these regression equations are given below:

$$\log k = -2.351 - 7.400 \times 10^{-3}B \quad (2)$$
$$(0.240) \quad (1.86 \times 10^{-3})$$
$$R = 0.740, \quad SE = 0.260, \quad n = 15$$

$$\log k = -2.697 - 0.976\beta \quad (3)$$
$$(0.362) \quad (0.548)$$
$$R = 0.511, \quad SE = 0.358, \quad n = 11$$

$$\log k = -3.687 + 0.592\pi^* \quad (4)$$
$$(0.458) \quad (0.622)$$
$$R = 0.272, \quad SE = 0.40, \quad n = 13.$$

So to the above single parameter equations a second parameter is added and the regression analysis is carried. The following are some of the results:

$$\log k = -2.294 - 7.520 \times 10^{-3}B - 5.954 \times 10^{-2}Y \quad (5)$$
$$(0.393) \quad (2.771 \times 10^{-3}) \quad (9.701 \times 10^{-2})$$
$$R = 0.754, \quad SE = 0.277, \quad n = 14$$

$$\log k = -2.340 - 7.440 \times 10^{-3}B - 1.961 \times 10^{-3}E \quad (6)$$
$$R = 0.744, \quad SE = 0.282, \quad n = 14$$

$$\log k = -2.549 - 10.042 \times 10^{-3}B + 0.818\pi^* \tag{7}$$
$$R = 0.846, \quad SE = 0.234, \quad n = 13$$

TABLE-1

THE PSUEDO FIRST ORDER RATE CONSTANTS AND THE SOLVATION PARAMETERS USED IN THE OXIDATION OF BENZYL ALCOHOL BY QUINOLINIUM DICHROMATE

[Benzyl alcohol] = 5.00×10^{-1} mol dm^{-3}; [QDC] = 1.00×10^{-3} mol dm^{-3}; T = 303 K

Solvent	$k \times 10^4$ sec^{-1}	B	P	π^*	$k_{cal} \times 10^4$ sec^{-1}
Formamide	6.47	140	0.211	0.97	7.53
Dimethyl formamide	2.13	166	0.211	0.88	3.47
Dimethyl sulfoxide	2.89	193	0.221	1.00	2.07
Acetone	9.47	116	0.169	0.60	7.44
Methanol	7.88	119	0.169	0.60	7.44
Ethanol	6.22	124	0.181	0.54	4.64
n-Propanol	2.49	120	0.190	0.51	4.07
t-Butanol	1.63	132	0.191	0.41	2.24
Ethoxyethanol	6.65	125	0.196	0.71	6.07
Acetonitrile	15.11	103	0.174	0.75	15.78
Benzonitrile	14.87	90	0.235	0.90	13.70
Acetic acid	4.33	98	0.226	—	—
Water	4.32	123	0.219	—	—
Chloroform	21.41	35	0.265	0.76	20.78
Ethyl acetate	1.26	181	0.185	0.55	1.20

Though there is some increase in the strength of the correlation due to the addition of second parameter, the correlation is not satisfactory. Now the analysis is repeated by introducing a third parameter, which results in the following relations:

$$\log k = \underset{(0.539)}{-2.720} - \underset{(2.691 \times 10^{-3})}{9.713 \times 10^{-3}B} + \underset{(0.463)}{0.932\pi^*} + \underset{(0.246)}{0.124\alpha} \tag{8}$$
$$R = 0.840, \quad SE = 0.256, \quad n = 11$$

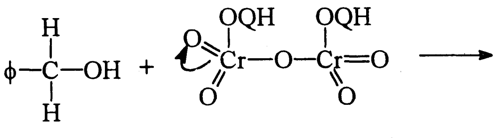
$$\log k = \underset{(0.451)}{-2.703} - \underset{(2.577 \times 10^{-3})}{9.702 \times 10^{-3}B} + \underset{(0.399)}{0.866\pi^*} + \underset{(1.535 \times 10^{-2})}{1.209 \times 10^{-2}E} \tag{9}$$
$$R = 0.866, \quad SE = 0.245, \quad n = 12$$

$$\log k = \underset{(0.565)}{-1.635} - \underset{(1.609 \times 10^{-3})}{10.101 \times 10^{-3}B} - \underset{(2.797)}{6.372P} + \underset{(0.377)}{1.309\pi^*} \tag{10}$$
$$R = 0.913, \quad SE = 0.189, \quad n = 13$$

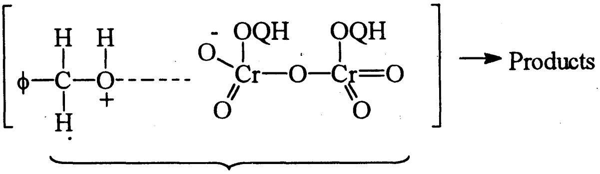
This data indicates that there is a remarkable increase in the strength of relation when the solvent parameters B, P and π^* are used. The correlation coefficient is 0.914 explaining 83.37 % of the data. The validity of this equation is also tested by subjecting the data to F-test and t-test[7]. F_{cal} (15.0) is greater than the table value at 1% level of significance. The t-test suggests that the parameters B and π^* are significant at 99% confidence levels and the parameter 'P' is significant at 95% confidence level. We can draw the following conclusions from the above relation, *i.e.*, equation (10).

- The reaction is influenced by three solvation parameters, nucleophilicity (B), polarisability (P) and π^* which is a measure of the ability of the solvent to stabilize a charge or a dipole.
- The negative coefficient of B in equation (10) suggests that the reactants are more solvated than the transition state due to nucleophilicity of the solvent.
- The reactants are also more solvated due to polarisability of the solvent compared to the transition state as indicated by the negative coefficient of P.
- The transition state is more solvated due to the ability of the solvent to stabilize the dipole which is measured by π^* as evidenced by the positive coefficient of this parameter in the above equation.

Considering these points the mode of solvation can be represented as follows.



Solvation due to nucleophilicity and polarisability of the solvent



Solvation by stalilization of dipole

The validity of equation (10) is further tested[7] by calculating the rate constants (Table-1) in each solvent using the above equation and plotting a graph between k_{cal} and k_{obs}. This is a straight line with a slope of 0.989 and the correlation coefficient r is 0.99.

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