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SOLVATION MODELS IN THE REACTION BETWEEN ALLYLBROMIDE AND DIPHENYLAMINE

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ABSTRACT

The effect of different protic and dipolar aprotic solvents on the rate of the reaction between allylbromide and diphenylamine has been studied. Correlation of the rate constants with different solvent parameters indicates that the polarity (Y), polarisability (P) and electrophilicity (E) of the solvent simultaneously influence the rate and solvation of the reactants and transition state is due to these properties of the solvent.

***Keywords**: Allylbromide, Diphenylamine, LSER, Solvent parameters, Differential solvation free energy.*

INTRODUCTION

A solvent influences the rate of reaction by solvating the reactants and the transition state due to dipolar effect[1]. The solvent-solute interactions are of two types, namely specific and non-specific[2]. The specific solvent-solute interactions are short range forces and are chemical in nature. These interactions primarily occur when a solvent interacts with the solute, by donating or accepting an electron pair or by forming hydrogen bonds. The intensities of these interactions are measured in terms of electrophilicity (E)[3], nucleophilicity (B)[3], hydrogen bond donor ability (α)[4] and hydrogen bond acceptor ability (β)[4] of the solvent. In addition to these interactions, all the solvents are able to interact with the reactants and transition state non-specifically due to coulombic and inductive forces. These are long range forces and the intensities of these interactions are measured in terms of polarity (Y)[5] and polarisability (P)[5] of the solvent. So the general term polarity of the solvent means the overall solvation ability of the solvent due to either all or some of these properties. Hence the effect of solvent on reaction rate has to be represented not by a single parameter equation but by a multiparametric equation[6] according to equation 1

$$\log k = \log k_0 + yY + pP + bB + eE \ldots\ldots\ldots \qquad (1)$$

where k is rate constant of the reaction in any solvent, k_0 is the rate constant in an inert solvent, which does not solvate at all, taken as the reference state. Y, P, B and E are the different solvation parameters of the solvent under consideration. The coefficients y, p, b and e are the susceptibilities of k to the respective solvent-solute interaction parameters. From the regression analysis and the signs of these coefficients we can get an idea about the nature and extent of solvation of the reactants and transition state. The results on such studies have been reported[7-17] earlier using different nucleophiles and substrates. With the help of this, one can suggest the specific site of solvation and hence the solvation model. Keeping this in view, the authors studied the reaction between allylbromide and diphenylamine in ten different solvents and the results are presented.

EXPERIMENTAL

Allylbromide and the nucleophile diphenylamine were purchased from Merck and were used as such. The solvents methanol, ethanol, *n*-propanol, *i*-propanol, benzylalcohol, acetone, acetonitrile, formamide, N,N-dimethylformamide and dimethyl sulfoxide were purchased from Sd fine A.R. grade and were used after purification by literature methods.

The solutions of diphenylamine were prepared by dissolving the required weighed quantity in these solvents. The reactions were initiated by mixing the thermally equilibrated solutions allylbromide and diphenylamine at appropriate temperatures. The progress of the reaction was followed by measuring the conductance of the reaction mixture at different time intervals using a digital conducitivity bridge (CENTURY make). The reactions were conducted in different solvents in temperature range 303 to 318K. The reaction rates at different concentrations of allylbromide and diphenylamine indicated that the reaction is overall second order with first order dependence each on [allylbromide] and [diphenylamine]. The reactions were conducted at [allylbromide] = [diphenylamine] = 0.02mol dm^{-3} and the second order rate constants (k) were determined from the slopes of linear plots obtained when was plotted against time, where C_t and C_∞ are conductance of the reaction mixture at t and infinite time intervals. The validity of the corresponding multiparmetric equations obtained was tested by applying the statistical F-test and Student t-test[18].

The product separated after completion of the reaction (from the methanol extract) has a melting point of 145 °C. The IR (with KBr) spectrum of this compound indicates the absence of absorption band around 3200 cm^{-1} $\frac{C_\infty}{C_\infty - C_t}$ (due to N-H) and presence of a band around 2800 cm^{-1} (due to N-CH$_2$)[19] suggesting the formation of N-allyldiphenylamine.

RESULTS AND DISCUSSION

The second order rate constants k, determined in ten different protic and aprotic solvents are presented in Table 1. Correlation of these log k values with different solvent parameters, namely polarity (Y), polarisability (P), solvent electrophilicity (E), solvent nucleophilicity (B), hydrogen bond donor ability (α), hydrogen bond acceptor ability (β) and specific polarization (π^*) does not give satisfactory results. The corresponding correlation coefficients are 0.85, 0.15, 0.22, 0.56, 0.39, 0.05 and 0.53 respectively.

Then the data are analyzed taking two significant parameters each time. Some of the successful correlations obtained are given below.

1) $\log k = -13.55 + 22.63\,Y - 0.13\,\beta$; $R = 0.85$
$(2.45) \quad (5.17) \quad (0.40) \qquad (0.22)$

2) $\log k = -12.79 + 19.82\,Y - 3.55 \times 10^{-3}\,B$; $R = 0.88$
$(2.33) \quad (5.24) \quad (2.80 \times 10^{-3}) \qquad (0.18)$

3) $\log k = -13.48 + 22.59\,Y - 0.01\,E$; $R = 0.88$
$(2.23) \quad (4.71) \quad (0.01) \qquad (0.20)$

4) $\log k = -13.05 + 21.69Y - 0.31\,\alpha$; $R = 0.90$
$(2.04 \quad (4.31) \quad (0.17) \qquad (0.18)$

5) $\log k = -15.35 + 24.01\,Y + 5.40\,P$; $R = 0.90$
$(2.19) \quad (4.28) \quad (2.82) \qquad (0.18)$

6) $\log k = -13.05 + 20.32Y + 0.67\pi^*$; $R = 0.91$
$(1.91) \quad (4.14) \quad (0.30) \qquad (0.17)$

The values in parentheses are standard errors of the coefficients determined.

Though there is improvement in the correlation coefficient (R) these relations explain only 72-83% of the data. Then a third parameter is introduced in the above linear solvation energy relationship (LSER). The resultant equations obtained are

$$\begin{array}{llllll} 7) & \log k = -14.99 & +\ 23.23\,Y & +\ 4.86\,P & +\ 0.79 \times 10^{-3}\,B & ;\quad R = 0.90 \\ & (2.84) & (5.72) & (3.86) & (3.50 \times 10^{-3}) & (0.20) \\ & t = -5.26 & 4.06 & 1.25 & 0.22 & \\ 8) & \log k = -12.83 & +\ 19.69\,Y & +\ 1.21 \times 10^{-3}\,B & +\ 0.60\,\pi^{*} & ;\quad R = 0.91 \\ & (2.11) & (4.72) & (2.99 \times 10^{-3}) & (0.34) & (0.18) \\ & t = -6.09 & 4.18 & 0.40 & 1.63 & \\ 9) & \log k = -15.15 & +\ 23.95\,Y & +\ 5.25\,P & -\ 0.02\,E & ;\quad R = 0.93 \\ & (2.05) & (4.01) & (2.64) & (0.01) & (0.17) \\ & t = -7.37 & 5.96 & 1.98 & -1.41 & \end{array}$$

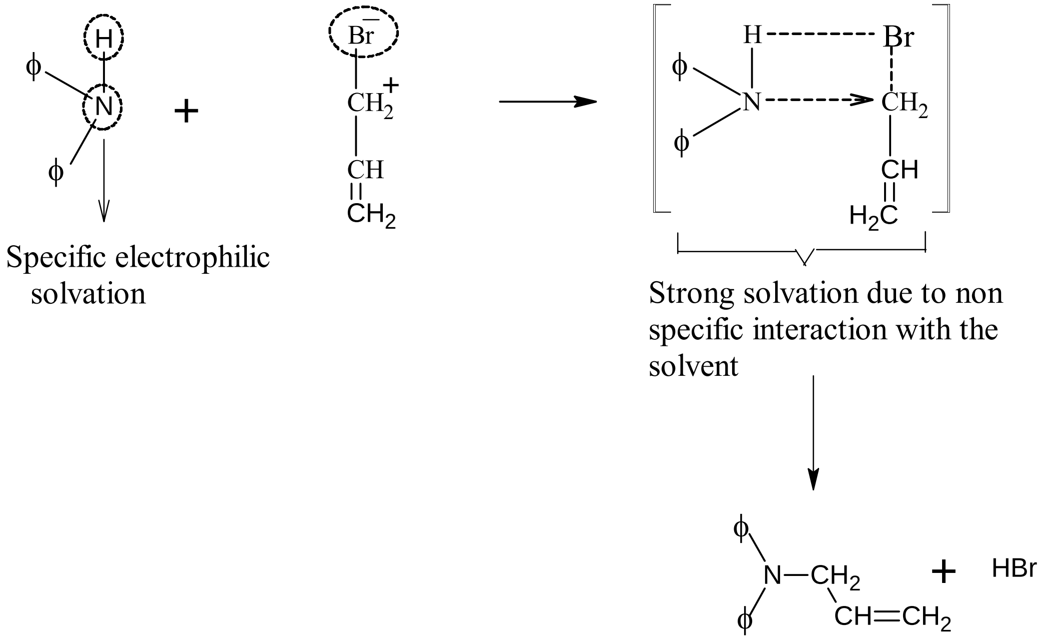
The above equation (equation 9) with a correlation coefficient of 0.93 suggests that log k correlates well with polarity, polarisability of the solvent and a specific parameter E i.e. electrophilicity of the solvent. The analysis could not be extended by including a fourth parameter since there are no sufficient data points. The R value of 0.93 suggests that, 86% of the experimental results can be explained by this equation. To know whether this is a meaningful correlation or not, the data is subjected to F test. F_{cal} is 12.94 while F_{table} is 9.78[20] significant at 1% level. This higher value of F_{cal} indicates the validity of the above equation. The significance of the independent variables used in the above LSER is verified by student t-test. The parameter Y is significant at 99% confidence level, P is significant at 95% confidence level and E is significant at 90% confidence level. Further, there is an excellent correlation between log k_{obs} and log k_{cal} with a slope of 1.00 and a correlation coefficient (R) of 0.99.

The contributions of these three parameters in the LSER are found to be Y = 64%, P = 21% and E = 15%.

The following conclusions, regarding the mode of the solvation of the reactant and the transition state, can be drawn from the above LSER.

1. The rate of the reaction is strongly influenced by one of the non-specific parameters, which is a measure of the polarity of the solvent. A positive value of the coefficient of Y in the above LSER suggests that, the transition state is more solvated than the reactants due to long range interactions with the solvent.
2. The reaction rate is influenced by polarisability P of the solvent. Increase in polarisability increases the rate. A positive value of the coefficient of this parameter in the LSER suggests that the transition state is more solvated than the reactants.
3. Solvent electrophilicity E also influences the rate. The negative coefficient of E in the LSER indicates that the reactants are more solvated than the transition state due to this property.

In view of these observations the following solvation model is proposed for the reaction of allylbromide with diphenylamine (Scheme 1).



Scheme-1

In the reaction between diphenylamine and benzylbromide carried in thirteen different protic and aprotic solvents[14] it was observed that the solvation of the reactants and the transition state is due to a non-specific property Y and specific nucleophilicity and hydrogen bond donor ability of the solvents.

From the temperature effect on the rate data, the energy of activation E_a, enthalpy, entropy and free energy of activation $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ are computed and presented in Table 1. The $\Delta S^{\neq}$ evaluated in different solvents indicate that these are highly dependent on the nature of the solvent. Except in *i*-propanol, dimethyl sulfoxide and formamide there is overall more solvation of the transition state than the reactants. The $\Delta G^{\neq}$ computed is nearly constant (91.42±2.89 $kJmol^{-1}$), suggesting a unified reaction scheme in all solvents. The differential free energy $\delta\Delta G^{\neq}$ values computed taking methanol as the reference solvent are all negative except for *n*-propanol suggesting that the reaction system is more stabilized when it is changed from methanol to other solvents.

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Table 1: Second order rate constants and Thermodynamic parameters
[Allylbromide – Diphenylamine system]
[AlBr] = [DPA] = 0.02 M

Solvent	k x 10^4 dm^3 mol^{-1} s^{-1} at temp/K				Ea ($kJmol^{-1}$)	* $\Delta H^{\neq}$ ($kJmol^{-1}$)	* $\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)	*$\Delta G^{\neq}$ ($kJmol^{-1}$)	$\delta\Delta G^{\neq}$ ($kJmol^{-1}$)
	303	308	313	318					
Methanol	5.12	11.10	30.10	39.21	95.70	93.18	-0.72	93.41	0.00
Ethanol	10.12	19.50	27.51	45.81	76.58	74.06	-57.50	91.49	-1.91
n-Propanol	3.34	6.61	10.21	14.15	82.05	79.53	-49.20	94.44	1.04
i-Propanol	6.64	9.15	20.54	40.02	114.88	112.36	64.88	92.70	-0.70
Dimethyl sulfoxide	33.28	116.10	200.10	341.01	91.90	89.38	2.43	88.65	-4.75
Dimethyl formamide	11.14	19.15	27.26	37.50	64.60	62.08	-96.84	91.42	-1.98
Formamide	25.16	83.01	105.10	166.10	109.13	106.61	55.44	89.82	-3.58
Acetonitrile	16.64	24.08	30.21	57.50	57.44	54.92	-117.30	90.37	-3.03
Acetone	16.62	25.20	35.31	58.33	63.18	60.66	-98.07	90.38	-3.02
Benzyl alcohol	10.50	16.66	22.52	35.50	63.28	60.66	-101.88	91.53	-1.87

* at 303 K

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