LSER in the reaction between *p*-nitrobenzyl bromide and 2-mercaptobenzoxazole

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The reaction between *p*-nitrobenzyl bromide and 2-mercaptobenzoxazole has been studied by following the conductance of the reaction mixture at different time intervals. The reaction is overall second order, being first order with respect to both [nucleophile] and [substrate]. The reaction is studied in 14 different protic and dipolar aprotic solvents and the second order rate constants are determined. Correlation of rate constants with different solvent parameters indicated that electron pair accepting ability of the solvent (E) and hydrogen bond accepting ability (β) of the solvent simultaneously influence the rate of the reaction.

Keywords: *p*-nitrobenzyl bromide, 2-mercaptobenzoxazole, rate constant, linear solvation energy relationship

A literature survey[1-6] on the huge body of established experimental data of the effect of solvents on different physico chemical properties of molecules suggests that there are few mechanisms of interaction between solute and solvent. According to Reichardt[7] these interactions which result in solvation of the solute are of two types, namely specific and non-specific interactions. The non-specific interactions are long range interactions and the intensity of these interactions is measured interms of the polarity (Y) and the polarisability (P) of the solvent. The second category are specific interactions and are chemical in nature. During these interactions certain localised centres in the solvent molecules interact specifically with some localised centres of solutes and thus solvation occurs. The intensities of this type of interaction are measured in terms of Lewis acidity (E) Lewis basicity (B) and the hydrogen bond donor/acceptor ability (α/β) of the solvent. Therefore any physicochemical solvent-dependent property (X) can be represented as[8]

$$X = X_o + aA + bB + cC +$$

where X is the property in any solvent, X_o is the property in an inert solvent which does not solvate the solute at all, A, B, C *etc*. are measures of different solvation abilities of the solvent and a, b, c, d, *etc*. describe the susceptibility of X towards the respective solvation properties. Thus the mode of solvation can be deduced from this correlation equation which is known as the linear solvation energy relationship (LSER). Since a rate constant is a solvent-dependent property we have studied the effect of different protic and aprotic solvents on the nucleophilic substitution reaction between *p*-nitrobenzyl bromide and 2-mercaptobenzoxazole and correlated the rate constants with different solvent parameters. From the results of this correlation analysis a solvation model is proposed with the help of the LSER obtained.

Results and discussion

The second order rate constants, *k* determined in 14 different protic and dipolar aprotic solvents are presented in Table 1. Values of log *k* are correlated individually with the different solvent parameters Y,[9] P,[9] E,[10] α,[11] β[11] and π*.[11] The corresponding correlation coefficients 'r' are 0.22, 0.04, 0.67, 0.34, 0.28 and 0.22 respectively. These data suggest that log *k* is better correlated with E, α, β and Y compared to other parameters. Then the data are analysed taking two significant parameters each time. The successful correlation obtained is given below.

$$\log k = -3.24 + 1.63\,\beta + 0.11\,E \; ; R = 0.92$$
$$(0.22) \quad (0.34) \quad (0.02)$$

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The values in parentheses are standard errors and R is the linear multiple correlation coefficient. The above data suggest that, the strength of the correlation increases with an explained variance of 85 % when E and β are included in the analysis.

This relation explains 85 % of the data and the linear multiple correlation coefficient is R = 0.92. F_{cal} (43.7) is greater than F_{table} (7.2)[13] at 1 % level of significance.[12]

The significance of the parameters used in the above equation is tested by *t*-test.[12] Comparison of t_{cal} with t_{table} values[13] indicates that both the parameters E, and β are significant at 99 % confidence level. Further there is excellent correlation between log k_{obs} and log k_{cal} with a slope 1.00 and correlation coefficient r = 0.99. Since solvent parameters used in the above equation E and β do not vary numerically by the same magnitude, the corresponding coefficients are normalised and the percentage contribution of each solvent parameter towards the observed rate data is calculated.

The following conclusions can be drawn from the above LSER.

1. The rate of the reaction is strongly influenced by E, the electron pair accepting ability of the solvent. The positive coefficient of this parameter in the LSER suggests that the transition state is more solvated than the reactants due to the electrophilicity of the solvent. The contribution of this term in the above relationship is 63 %.
2. The hydrogen bond accepting ability of the solvent also influences the rate. The transition state is more solvated by donating a hydrogen bond to the solvent. The contribution of this parameter, β, is only 37 %.

The validity of this relationship of log *k* with E and β is now established.

The primary requirement to apply a biparametric equation is that there must be a poor correlation between the parameters used in the LSER. Analysis indicates that

$$E = -0.89 + 12.17\,\beta \; ; r = 0.45$$
$$(4.02) \quad (5.75)$$

The values in parentheses are standard errors and r is the correlation efficient.

This poor correlation between E and β suggests that the above LSER derived is not invalidated by a linear relationship between E and β.

The thermodynamic parameters E_a, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ computed and presented in Table 1 suggest that these are also strongly influenced by the solvents. The free energy of activation $\Delta G^{\neq}$ is nearly constant (88.75 ± 3.83 kJ mol^{-1}) indicating the operation of a similar type of mechanism in all the solvents used.

Table 1 Second order rate constants and thermodynamic parameters [benzyl bromide – 2-MBOZ system] [benzylbromide] = [2-MBOZ] = 2.00 x 10⁻² mol/dm⁻³ at 303 K

Solvent	$k \times 10^4$/dm³ mol⁻¹ s⁻¹ at T K				E_a	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$\Delta G^{\neq}$
	293	298	303	313	(kJ mol⁻¹)	(kJ mol⁻¹)	(JK⁻¹ mol⁻¹)	(kJ mol⁻¹)
Methanol	1.12	2.18	4.26	18.2	102.3	99.8	29	90.9
n-butanol	2.87	4.42	8.08	19.4	88.8	86.3	−16	91.3
Benzyl alcohol	0.51	0.85	1.67	3.37	94.1	91.7	6	89.9
Dimethyl sulfoxide	8.42	10.6	15.5	–	33.5	31.1	−193	89.4
i-propanol	2.67	6.58	19.3	107.5	135.7	133.2	146	88.9
n-propanol	1.25	3.33	7.11	27.1	108.8	106	52	90.4
Acetonitrile	0.94	1.67	5.80	13.7	99.4	96.9	14	92.5
Benzonitrile	17.5	22.5	41.0	66.8	50.6	48.1	−128	87.0
Acetone	4.69	10.5	18.0	26.7	48.5	46.0	−142	89.1
Ethylmethyl ketone	9.33	12.8	17.8	24.9	45.6	43.1	−168	85.8
Cyclohexanone	11.8	20.5	40.0	148	92.1	89.6	10	86.6
Dimethyl formamide	6.56	12.4	22.1	51.8	78.7	76.2	−31	85.7
t-butanol	36.5	84.2	163	208	48.5	46.0	−140	84.8
i-butanol	6.42	12.5	20.6	54.5	74.6	72.1	−63	90.1

From these results the following solvation model can be proposed for the transition state:

HBD solvation (β)   Electron pair acceptor solvation (E)

X = p-NO₂ C₆H₅
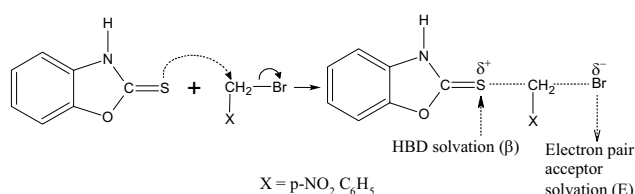
Experimental

p-Nitrobenzyl bromide (RIEDEL) and 2-mercaptobenzoxazole (ALDRICH) were used without any further purification. The solvents methanol, *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *t*-butanol, benzyl alcohol, acetonitrile, benzonitrile, dimethyl sulfoxide (Sd fine), dimethyl formamide, acetone, ethyl methyl ketone and cyclohexanone were used after distillation following literature methods[14]. The stock solutions of 2-mercaptobenzoxazole and *p*-nitrobenzyl bromide were prepared by dissolving the required weighed quantities in appropriate solvents. The solution of the substrate *p*-nitrobenzyl bromide was prepared only 30 minutes before initiating the reaction to prevent the solvolysis of the compound. The reactions were started by mixing the thermally-equilibrated reactants. The preliminary study indicated that (1) The solvolysis rates were almost 100 times less than the rate of the substitution reaction. (2) HBr is one of the products of the reaction. (3) The reaction is overall second order with a first order dependence of rate on the concentration of each reactant. The reactions were studied at [substrate] = [nucleophile] = 0.02 mol dm⁻³ in each solvent by following the conductance of the reaction mixture at different time intervals. The second order rate constants were determined from the slopes of the linear plots obtained when C_t-C_o/C_x-C_t was plotted against time according to the equation.[15]

$$k = 1/at \quad \frac{C_t - C_o}{C_\infty - C_t}$$

Where, C_o, C_t and C_x were the conductances of the reaction mixture at 0, t and infinite time, a was the initial concentration of the reactants and 'k' is the second order rate constant. The reactions were conducted at different temperatures in the range 293–313 K and the rate constants were determined. The rate constants thus determined in duplicate runs were found to be reproducible within ±5 % error.

Product analysis

p-Nitrobenzyl bromide and 2-mercaptobenzoxazole were taken in equimolar proportions in 100 % methanol and kept for 24 hours for the reaction to go to completion. Then the solution was concentrated and the product was extracted with ether. This was evaporated and the solid obtained was recrystallised using a mixture of petroleum ether and benzene in the ratio 1: 3 (v/v) to give a brown crystalline solid (m.p. 201 °C). The IR spectrum (with KBr) shows absorption bands at 2720 cm⁻¹ and 1400 cm⁻¹ indicating the presence of the S-CH₂ group (literature values[16] are 2,700–2,600 cm⁻¹ and 1420 cm⁻¹). Another band at 700 cm⁻¹ confirms the presence of the C–S–C group (thio ether link). The ¹H NMR spectrum recorded shows the signal around δ = 2.5 indicating the presence of S-CH₂ protons.[17] These data tentatively suggest the formation of *S-p*-nitrobenzylmercaptobenzoxazole.

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