Effect of solvents and mode of solvation in the reaction between benzyl bromide and 2-mercaptobenzothiazole†

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The reaction between benzyl bromide and 2-mercaptobenzothiazole has been studied in different protic and aprotic solvents. The kinetic study shows that the reaction is second order with first order dependence each on [benzyl bromide] and [2-mercaptobenzothiazole]. Analysis of rate data shows that there is no direct correlation between the rate constant and dielectric constant of the solvent. Correlation of rate data with different solvent parameters like polarisability, nucleophilicity and hydrogen bond acceptor ability, using linear multiple regression analysis shows that the reaction is influenced by these properties of the solvent. From the regression coefficients, information on the mode of solvation of the reactants and the transition state is obtained. The reaction has also been studied at different temperatures and the thermodynamic parameters \( \Delta H^\circ \), \( \Delta S^\circ \) and \( \Delta G^\circ \) are computed.

Any solvent influences the rate of a reaction by solvating the reactants and the transition state. A substance is solvated due to two types of interactions with the solvent, namely, specific and non-specific interactions. All solvents interact with the substances non-specifically. The intensity of these non-specific interactions are measured in terms of polarity of the solvent \( P \) and polarisability \( y \) of the solvent. Specific solvation of the substance primarily occurs when the solvent interacts with a charged atom or group in a molecule. The intensity of these interactions is measured in terms of electrophilicity \( E \), nucleophilicity \( B \), hydrogen bond donor ability \( \alpha \) hydrogen bond acceptor ability \( \beta \) etc. So, the general term polarity of the solvent means the overall solvation ability of the solvent due to either all or some of the above properties of the solvent. Therefore, the effect of solvent on reaction rate is to be expressed not by a single parameter equation, but by a multiparameter equation, i.e.

\[
\log k = \log k_0 + aA + bB + cC + \ldots (1)
\]

where \( k \) is the rate constant of the reaction in any solvent and \( k_0 \) is the rate constant in a reference solvent which is inert. The coefficients \( a, b, c \) are the susceptibilities of \( k \) to the respective solvent parameters \( A, B, C \) etc. These coefficients indicate the relative solvation of the reactants over the transition state and the mode of solvation. With this end in view, the reaction between benzyl bromide and 2-mercaptobenzothiazole has been studied in fourteen protic and aprotic solvents and the results are presented.

Experimental

The solvents, methanol, ethanol, \( n \)-propanol, \( i \)-propanol, \( n \)-butanol, \( i \)-butanol, \( n \)-hexanol, benzyl alcohol, acetonitrile, benzonitrile, acetone, dimethyl sulphoxide and dimethylformamide were all of AR grade and were used after purification by literature methods. Benzyl bromide (Riedel) and the nucleophile, 2-mercaptobenzothiazole (Aldrich) were used as such.

The solutions of the reactants of required concentrations were prepared by dissolving known volume/weight of benzyl bromide/nucleophile in a known volume of the solvent.

The reaction was initiated by mixing thermally equilibrated solutions of the substrate and the nucleophile at the required temperature. The course of the reaction was followed by measuring the conductance of the reaction mixture at different time intervals using a Toshniwal conductivity bridge.

Measurement of rates at different concentrations of the substrate and the nucleophile showed that the reaction is overall second order, with first order dependence each on the [substrate] and the [nucleophile]. The second order rate constants were calculated using the relation:

\[
k = \frac{1}{at} \times \frac{C_t - C_0}{C_x - C_t}
\]

where \( C_0, C_t \) and \( C_x \) are the conductances of the reaction mixture at zero, \( t \) and infinite time intervals; \( a \) is the initial concentration of the reactants. The rate constants thus determined were found to be reproducible within 5% error. A PCL personal computer was used to carry out the multiple regression analysis. F-test and student t-test were used to know the validity of the bi- and tri-parameter equations obtained.

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Results and discussion

The second order rate constants determined from the slopes of the linear plots of \((\text{C}_x - \text{C}_y)^{-1}\) against time, in different solvents are presented in Table 1. Correlation of rate constants with the individual parameters of the solvent, \(E, Y, P, B, \beta, \pi^*\) and \(\alpha\) shows a poor correlation and the corresponding regression coefficients, \(r\), are 0.12, 0.11, 0.47, 0.20, 0.64, 0.46, 0.37 and 0.07 respectively. Then, the rate data is analysed using a biparameter equation which involves \(P\) and \(B\) since, there is a better correlation with these two parameters. This gives a satisfactory correlation with the multiple regression coefficient, \(R = 0.93\) explaining 86% variance of the observed data. The corresponding equation obtained is

\[
\log k = -1.408 - 17.97 P + 0.0155 B
\]

Std error 0.224 2.94 0.00237

...(2)

Then a third parameter \('\beta'\) is introduced into this equation and the result is

\[
\log k = -1.492 - 18.10 P + 0.0164 B - 0.6612 \beta
\]

Std error 0.28 2.91 0.0036 0.48

...(3)

There is a slight improvement in the regression coefficient, \((R = 0.95)\) explaining 91% variance of the observed data. Replacement of \(\beta\) in Eq.(3) by \(\pi^*\) which is a measure of solvation due to dipolar effects further improved the \(R\) value (0.97) with 95% explained variance of the observed data. The equation obtained from this analysis is

\[
\log k = 1.481 - 17.90 P + 0.0144 B + 0.982 \pi^*
\]

Std error 0.22 2.93 0.0038 0.50

...(4)

However, this analysis could not be extended by adding both \(\beta\) and \(\pi^*\) to the biparameter Eq. (2), as there are no sufficient data points to use four parameters.

From the above observations the following conclusions can be drawn.

(i) The reaction is influenced by \(P\), which is a measure of the polarisability of the solvent. The –ve sign of the coefficient of this term in Eqs 2-4 shows that the non-specific interaction between the reactants and the solvent is more than the transition state-solvent interaction.

(ii) Another term which successfully enters into the regression analysis is \(B\) suggesting that, nucleophilic solvents influence the rate. The +ve sign of the coefficient of this term indicates that the non-specific interaction between the reactants and the solvent is more than the transition state-solvent interaction.

(iii) \(\beta\), which is a measure of the hydrogen bond acceptor ability (HBA) of the solvent also influences the rate. The –ve sign of the coefficient of this parameter suggests that HBA solvents strongly solvate the reactants than the transition state and such solvents do not assist the formation of the transition state.

(iv) The transition state is also stabilized due to solvation by virtue of dipolar effects as indicated by the +ve coefficient of \(\pi^*\).
(v) There is no electrophilic solvation of the $-$ve end of the transition state, as the correlation with $E$, the electrophilicity of the solvent is very poor.

Considering these points the mode of solvation of the reactants and the transition state can be represented as in Scheme 1.

The second order rate constants evaluated at three different temperatures in the range 293 to 313 K and the corresponding thermodynamic parameters evaluated $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ are given in Table 2.

The inherent limitations in the applicability of multiparameter correlation of any reaction are that there should be at least some individual correlation between the rate constant and the parameters used in the multiparameter equation and the mechanism of the process under investigation should be similar in all the solvents studied. The free energy of activation, $\Delta G^\circ$ determined in all the solvents studied is nearly constant ($88.0 \pm 3.0$ kJ mol$^{-1}$), suggesting the operation of a unified mechanism in all the solvents used. The product separated and analysed (TLC analysis) shows that the same product is obtained in both protic and aprotic solvents.

References
1 Christian Reichardt, Angew Chem. 18 (1979) 98.