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Solvent Effects on Rates of Base-catalysed Condensation of *o*-, *m*- & *p*-Hydroxybenzaldehydes with Acetone

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The effect of changing dielectric constant (*D*) of the medium on the rates of base-catalysed condensation of *o*-, *m*- and *p*-hydroxybenzaldehydes with acetone has been studied by using different aquo-alcoholic mixtures of methanol, ethanol and isopropanol, at different temperatures. The rates of condensation decrease with decreasing *D* up to 60% v/v of ethanol and isopropanol and later remained either constant or slightly increase. In the case of methanol, the rates however decreased throughout. Plots of log *k*″ vs 1/*D* are linear with negative slope up to 60% v/v of ethanol and isopropanol and up to 90% v/v of methanol. Thermodynamic parameters and activation energies in isodielectric mixtures were calculated.

It was reported earlier that the base-catalysed condensation of aromatic aldehydes with ketones takes place via the formation of intermediate secondary alcohols (ketols) and involves several equilibria[1-4]. Also from substituent effect studies, it was concluded that the ketone anion reaction with aldehyde molecule is the rate determining step. To confirm this, solvent effect studies have been carried out on the formation of different chalkones in various aquo-organic solvent mixtures (aquomethanol, ethanol and isopropanol) in the present work.

Materials and Methods

Organic solvents were purified by standard methods[5]. The dielectric constants of the aquo-alcoholic mixtures were obtained from literature[6]. The methods employed for following the rates are as described in our previous work[2].

Results and Discussion

In the condensation 4-hydroxy benzaldehyde with acetone the rate decreased with decreasing dielectric constant (*D*) in the case of water-methanol mixtures. However, in the cases where water-ethanol and isopropanol mixtures were used the rates decreased up to 60% (v/v) of alcohol and later remained either constant, or increased slightly with increasing percentage of alcohol, depending on the nature of aldehyde used. The plots of log *k*″ vs 1/*D* where *k*″ is bimolecular rate constant, were linear with a negative slope up to 60% (v/v) of all alcohols studied (Fig. 1). The slopes of these plots decreased from methanol to isopropanol at constant temperature. Above 60% (v/v) of ethanol or isopropanol, the plot was almost parallel to X-axis in the case of 3-OH and 4-OH benzaldehydes, while it was linear with a positive slope in the case of 2-OH-benzaldehyde.

The negative slope of the plot of log *k*″ vs 1/*D* could be explained on the basis of Amis equation[7], for an ion-dipole type of reaction. The linear plot

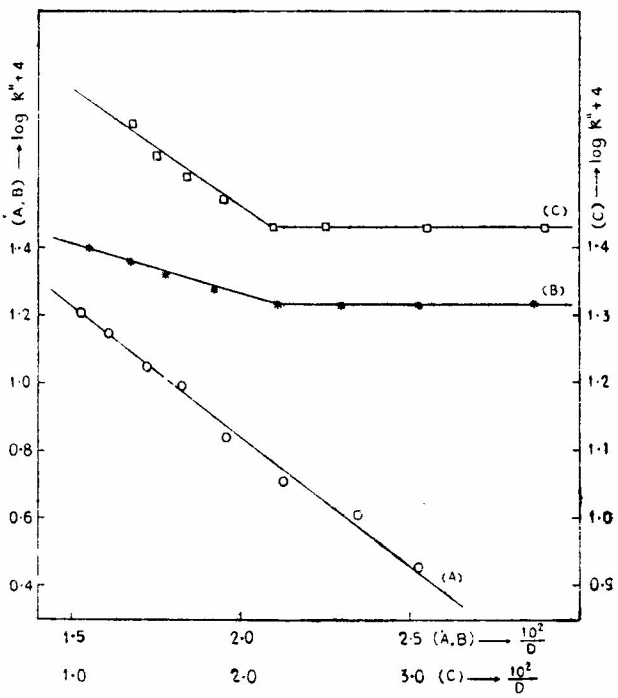

Fig. 1 — Plots of log *k*″ versus 1/*D* {Effect of (A) [methyl alcohol]; (B) [ethyl alcohol]; and (C) [isopropyl alcohol]}

with negative slope indicates that the reaction could be between a negative ion and a dipole. This is in favour of the slow step suggested in the mechanism for the condensation of an aldehyde with a ketone anion.

The significant change in the trend of decreasing rate constants with decreasing *D* beyond 60% (v/v) of ethyl or isopropyl alcohol could be explained on the basis of reaction (1) which may be taking place in the reaction mixture.

$$OH^- + ROH \rightleftharpoons H_2O + OR^- \quad ...(1)$$

According to reaction (1) at higher [alcohol] (above 60% v/v), the OR^- produced, whose basic strength

differs from alcohol to alcohol, might be affecting the rate of condensation. Since methanol and water have the same pK_a values[8], OMe^- produced may be expected to have almost same basic strength in these two media. Hence, even if OMe^- acts as a new catalyst, it is not going to affect the rate of the reaction. So, at higher percentage of methanol, it is probably dielectric constant effect that is predominating and hence the decrease in the rate.

However, in ethanol and isopropanol medium above 60% (v/v) of alcohol, OEt^- or $OCH(CH_3)_2^-$ formed being stronger bases than either OMe^- or OH^-, might act as better catalysts than OH^- thus increasing the rate of condensation. In solutions of ethyl or isopropyl alcohol, therefore, there are two opposing trends. On one hand the increase in percentage of alcohol (decrease in D) decreases the rate, while on the other, the OR^- formation at higher percentages of alcohol increases the rate. In the case of 3-OH and 4-OH-benzaldehydes these two effects appear to cancel each other, such that the rate, above 60% (v/v) of ethyl or isopropyl alcohol, remains practically constant. If OR^- effect is higher, it might more than compensate for the dielectric constant effect, resulting in an increase in rate as in the case of the reaction of 2-OH-benzaldehyde with ketones. The increase in rate was much more prominent when isopropanol was used probably because the $OCH(CH_3)_2^-$ is better base than OEt^- or OMe^-.

The activation energies for the overall reaction increase with increase in percentage of alcohol for all alcohols. In the case of ethyl and isopropyl alcohols the $\Delta E^{\ddagger}$ values increased up to 60% v/v of alcohol and latter remained constant. The increase in $\Delta E^{\ddagger}$ may be attributed to greater solvation of the reactants as compared to the activated complex. The activation energy values along with other thermodynamic parameters obtained for all solvent mixtures are presented in Table 1.

The thermodynamic parameters for all the reactions studied in different solvent mixtures may be explained on the basis of isokinetic relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values obtained for different aquo-alcoholic mixtures. For example, for the condensation reaction of 4-OH-benzaldehyde with acetone the plots of $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ were linear for all the solvents used (up to 60% of ethyl or isopropyl alcohol and up to 90% of methyl alcohol), in accordance with the isokinetic equation[9].

$$\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \beta \Delta S^{\ddagger} \qquad \ldots(2)$$

The isokinetic temperature (β) values for methanol, ethanol and isopropanol are 350°, 346° and 348°K respectively and the corresponding experimental range of temperature used is 303-318°K. It is evident from these results that the β-value obtained is well above the experimental temperature range indicating that it is an enthalpy controlled reaction. This view gets further support from the data in Table 1 where activation energy for the fastest reaction is lowest and vice-versa.

The experimental activation energies involve a highly mixed dependence of the rate constant on temperature and dielectric constant of the medium.

TABLE 1 — VALUES OF ACTIVATION PARAMETERS AT DIFFERENT [ALCOHOL]

{[Aldehyde] = [acetone] = 0·025M; [OH^-] = 0·2M; temp. = 40°}

Alcohol %(v/v)	$\Delta E^{\ddagger}$ kcal mole^{-1}	$\Delta H^{\ddagger}$ kcal mole^{-1}	$\Delta G^{\ddagger}$ kcal mole^{-1}	$-\Delta S^{\ddagger}$ e.u.
		MeOH		
20	8·5	7·5	22·3	48·0
30	10·5	9·3	22·4	42·0
40	12·1	10·9	22·5	37·3
50	14·5	13·1	22·6	30·3
60	16·2	15·0	22·8	25·2
70	18·3	17·1	23·0	19·0
80	20·2	19·0	23·2	13·4
90	22·3	21·1	23·4	7·5
		EtOH		
20	11·5	10·3	22·0	37·6
30	13·2	12·0	22·1	32·3
40	15·3	14·1	22·2	25·8
50	17·4	15·2	22·2	22·5
60	19·1	17·9	22·3	14·0
70	19·1	17·9	22·3	14·0
80	19·1	17·9	22·3	14·0
90	19·1	17·9	22·3	14·0
		ISOPROPANOL		
20	14·8	13·6	21·8	26·3
30	16·5	15·3	21·9	21·0
40	18·3	17·1	21·9	15·4
50	20·1	18·9	21·9	9·8
60	22·0	20·8	22·0	3·9
70	22·0	20·8	22·0	3·9
80	22·0	20·8	22·0	3·9
90	22·0	20·8	22·0	3·9

Error limits for $\Delta E^{\ddagger}$ and $\Delta S^{\ddagger}$ are $\pm$0·85 kcal mole^{-1} and $\pm$2·5 e.u. respectively.

TABLE 2 — E_d VALUES FOR THE REACTION BETWEEN 4-OH-BENZALDEHYDE AND ACETONE IN METHYL, ETHYL AND ISOPROPYL ALCOHOLS

Alcohol	E_d (kcal mol^{-1}) at different D values (%, v/v)			
	60	56	52	48
Methyl alcohol	11·3	13·3	15·5	17·7
Ethyl alcohol	13·2	15·3	17·4	18·9
Isopropyl alcohol	15·0	17·1	19·2	21·1

In order to obtain a more precise treatment of the results, the temperature dependence of the D should be eliminated. This was achieved by calculating the activation energies for isodielectric mixtures of the various solvents used, from the corresponding rate constants in isodielectric solutions. The latter was obtained by interpolation, at chosen values of D, from plots of log k'' against $1/D$. The activation energy values, E_d, were then computed from the Arrhenius plots. The contribution due to solvation phenomenon could be considered more or less constant in these values. The values of E_d for alkaline condensation of 4-OH-benzaldehyde with acetone below 60% (v/v) of all alcohols are given

in Table 2, from which it is clear that the E_d values increase with decreasing dielectric constant irrespective of the nature of the alcohol.

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