SOLVENT EFFECT ON THE KINETICS OF BASE-CATALYSED CYCLIZATION OF 1,5-DIANILINO-2,4-DIPHENYLPENT-1,4-DIENE-3-ONE

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The kinetics of the base-catalysed cyclization of 1,5-dianilino-2,4-diphenylpent-1,4-diene-3-one to substituted 4-pyridone and aniline has been studied in aqueous dioxan mixtures in the temperature range 25-40°. The wt % of dioxan ranged from 45.73 to 72.59. The concentration of the KOH catalyst was fixed at 0.03 M. The reaction rate showed an increase with increasing dioxan content. The activation energy increased in the same direction. The results were discussed in the light of the thermodynamic parameters of activation. $\triangle G^{\neq}$ increased slightly as the water content increased while $\triangle S^{\neq}$ acquired a more negative value. Changes in $\triangle H^{\neq}$ and $\triangle S^{\neq}$ were attributed to specific solvation effects. The effect of dielectric constant on the reaction rate was discussed.

Key words: Solvent effect, Base catalysed, Heterocyclization.

INTRODUCTION

One of the most quantitative routes reported for the synthesis of 4-pyridone derivatives is the cyclization of substituted 1,5-diamino-pent-1,4-diene-3-one [1]. The cyclization took place by the action of acids or bases. The kinetics and mechanisms of the acid-catalysed [2] and base-catalysed [3] cyclization have been studied. In alkaline solutions, kinetic studies revealed that the reaction is first order with respect to each of dianilino compound and the alkali. An $S_N i$ mechanism was suggested for the reaction. They study of the effect of solvent composition on the kinetics and mechanism of the base catalysed reaction forms the subject of this investigation.

EXPERIMENTAL

The dianilino compound [1] was recrystallized from benzenemethanol, m.p. 170°. Specpure dioxan was obtained as reported in literature [4]. Boiled conductivity water was used in the preparation of the solvent mixtures. A PMQ II ZEISS spectrophotometer equipped with constant temperature-circulating bath and cell housing was employed to measure the absorbance at $\lambda = 420$ nm as a function of time. At this wave length the products have zero absorbance. Solutions of the compound and alkali, both in the same solvent mixture with the required composition, were mixed after attaining thermal equilibrium and quickly transferred to the spectrophotometric cell. Kinetic experiments were performed in aqueous dioxan in the temperature range 25-40°. The wt % of dioxan ranged from 45.73-72.59. This was limited by the solubility of the reactants.

RESULTS AND DISCUSSION

Spectral measurements, after reaction completion (> 24 hours), verified that aniline and N-2,6-triphenyl 4-pyridone were the only reaction products in the different mixtures. Kinetic studies were performed under pseudo-first order conditions where the concentration of KOH represented a large excess with respect to that of the dianilino compound. The absorbance at zero time (A_o) was estimated by extrapolation. The pseudo-first order rate constant (k_{obs}) was determined from the linear plots of the equation:

$$\log \frac{A_o}{A} = \frac{k_{obs}}{2.303} t$$

k_{obs} being equal to the product of the second order rate constant, k_2, and [KOH].

Repeated runs under one and the same conditions resulted in rate constant deviation of about ± 1 %. The reported values are the average of 2 runs.

Results of measurements in 50 vol % water-dioxan mixtures containing different concentrations of KCl (0-0.11 M), showed no dependence of the rate on the ionic strength. The value of k_{obs} was almost constant = 0.041 min^{-1} in 0.0724 M KOH at 35°

Figure 1 is a representative example of the results obtained in different water-dioxan mixtures containing 0.03 M KOH. The initial concentration of the compound was constant = 4.3×10^{-5} M. The second order rate constant was obtained by dividing K_{obs} by [OH] and list in Table 1. The activation energies were graphically calculated from Arrhenius plots.
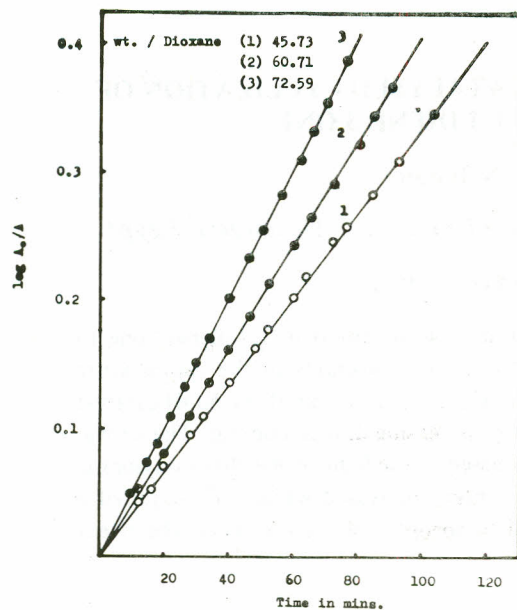
Fig. 1. Pseudo first order plots at 25°.

Table 1. Values of k_2 x 10^3 dm^3 mol^{-1} sec^{-1} and activation energy ($k J mol^{-1}$) in dioxan-water mixtures.

Wt % dioxan	45.73	50.74	55.73	60.71	65.67	70.62	72.59
Temp. = 25°	4.27	4.32	4.91	5.12	5.71	6.11	6.56
Temp. = 30°	6.17	6.58	7.24	7.83	8.72	9.78	10.48
Temp. = 35°	8.75	9.35	10.05	11.39	12.79	13.98	15.35
Temp. = 40°	12.79	13.29	15.25	16.57	18.63	21.18	23.22
E_a =	56.10	57.43	58.98	61.78	61.99	63.41	65.63

The rate constant showed an increase with increasing the dioxan content. The activation energy increased in the same direction. This unexpected trend may be explained if the effect of changing the solvent composition on the rate and mechanism is expressed in terms of the thermodynamic parameters of activation. The free energy of activation, $\triangle G^{\neq}$, was calculated from k_2 using Eyring equation [5]. The enthalpy of activation, $\triangle H^{\neq}$, was calculated from the experimental activation energy. The entropy of activation, $\triangle S^{\neq}$, was calculated from $\triangle H^{\neq}$ and $\triangle G^{\neq}$. These values are collected in Table 2.

$\triangle H^{\neq}$ and $\triangle S^{\neq}$ could be more sensitive indicators of the effect of solvent structure than the rate constant directly [6]. $\triangle H^{\neq}$ decreased with increasing the water content while $\triangle G^{\neq}$ slightly increased in the same direction. This might be largely due to linear compensation between $\triangle H^{\neq}$ and $\triangle S^{\neq}$ which is illustrated in Fig. 2. The increased stabilisation of the activated complex resulting from solvation by water molecules would produce the decrease in $\triangle H^{\neq}$. This is accompanied by a loss in the entropy of the

Table 2. Thermodynamic parameters of activition $\triangle G^{\neq}$ and $\triangle H^{\neq}$ in $k J mol^{-1}$, $\triangle S^{\neq}$ in $J mol^{-1} deg^{-1}$.

Wt % dioxan	45.73	50.74	55.73	60.71	65.67	70.62	72.59
$\triangle G^{\neq}$	87.95	87.86	87.53	87.45	87.15	86.99	86.82
$\triangle H^{\neq}$	53.63	54.97	56.51	59.31	59.52	60.94	63.16
$25^O \triangle S^{\neq}$	115.16	110.39	104.08	94.38	92.71	87.41	79.42
$\triangle G^{\neq}$	88.45	88.32	88.07	87.86	87.61	87.32	87.15
$30^O \triangle H^{\neq}$	53.59	54.93	56.47	59.27	59.48	60.90	63.12
$-\triangle S^{\neq}$	115.03	110.23	104.29	94.34	92.84	87.19	79.34
$\triangle G^{\neq}$	89.08	88.91	88.70	88.41	88.11	87.86	87.61
$35^O \triangle H^{\neq}$	53.55	54.88	56.43	59.23	59.44	60.86	63.08
$-\triangle S^{\neq}$	115.37	110.48	104.75	94.72	93.09	87.65	79.67
$\triangle G^{\neq}$	89.58	89.49	89.12	88.91	88.62	88.28	88.03
$40^O \triangle H^{\neq}$	53.50	54.84	56.39	59.19	59.40	60.82	63.03
$-\triangle S^{\neq}$	115.24	110.73	104.58	94.97	93.34	87.74	79.88
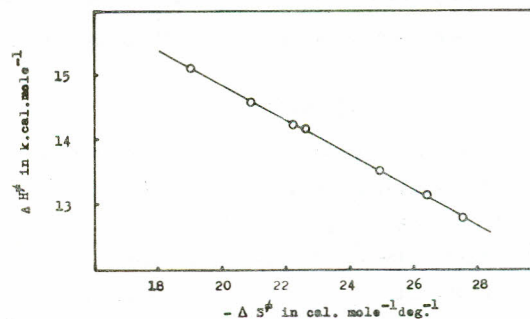
Fig. 2. Variation of $\triangle H^{\neq}$ with $\triangle S^{\neq}$ at 25°
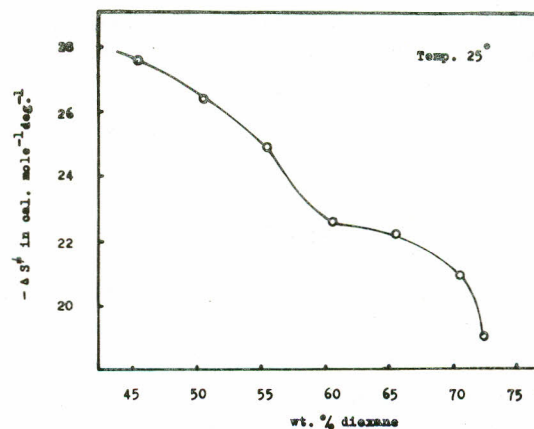
Fig. 3. Dependence of $\triangle S^{\neq}$ on solvent composition.

activated complex due to preferential orientation of the solvating molecules. Hence a more negative $\triangle S^{\neq}$ was expected with increasing the water content. Moreover, the observed linearity of $\triangle H^{\neq}$ and $\triangle S^{\neq}$ points to no changes in the reaction mechanism in the different solvent mixtures.

The non linear variation of $\triangle S^{\neq}$ with the solvent composition (Fig. 3) indicated specific solvation effects [7] and that the random distribution of the two components is not valid.

The effect of dielectric constant on the reaction rate was studied in the light of Laidler-Landskroener [8] and Amis [9] equations. The values of the dielectric constant of the solvent mixtures were obtained by interpolation from Akerlof's data [10]. Figure 4 shows the plots of log
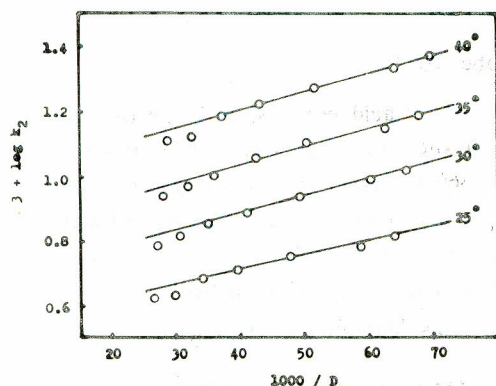

Fig. 4. Dependence of k_2 on dielectric constant.

k_2 versus $1/d$. Straight lines were obtained as predicted by the two equations. A slight deviation was observed in the higher dielectric constant mixtures. The positive sign of the slopes contradicts the negative one predicted by Amis equation [9] for an iondipole interaction:

$$\log k_{D=D} = \log k_{D=\infty} + \frac{Ze\mu}{kDTr^2}$$

Such contradiction was observed for some hydrolysis reactions in water-organic solvent mixtures [11-13]. Laidler-Landskroener equation [8] for ion-neutral mole-cule interaction in cases where the activated complex has a very large moment predicts no sign for the slope of log k versus $1/D$ plots.

$$\text{Slope} = \frac{e^2}{4.6kT} \left(\frac{1}{r_A} - \frac{1}{r^{\neq}} - \frac{3G^{\neq}}{2r^{\neq 3}} \right)$$

r_A is the radius of hydroxide ion and is taken as equal to 1.4×10^{-8} cm. [14]. Applying this equation, calculation of the radius of the activated complex led to a value of 2.95 Å.

The observed deviation from linearity could be attri-buted to the breakdown of the tetrahedral structure of water as a result of addition of dioxan [15]. This would affect the concentration of the free water molecules.

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