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Kinetics of cyclocondensation products of ketoazomethines and thioglycolic acid

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ABSTRACT : The kinetics of cyclocondensation of ketoazomethines (prepared by the condensation of phenyl glyoxal with aniline and para-diethyl amino-aniline) with thioglycolic acid in different experimental conditions of concentration, dielectric constant of medium, catalyst concentration and effect of temperature as typical examples for the new thiazolidinones have been proposed and related thermodynamic parameters have been calculated.

Keywords : Kinetics, Ketoazomethines, Thioglycolic acid.

I. INTRODUCTION

Comprehensive perusal of literature on chemical kinetics reveals that maximum kinetic studies have been conducted on oxidation reactions of organic compounds, viz. amines [1], amino acids [2,3], aldehydes [4], carboxy acids [5,6] and carbohydrates [7] whereas hydrolysis [8-10] and halogenations [11],oxidation [12] reactions of organic compounds have been comparatively less investigated. Kinetic studies on the synthesis of organic compounds [13-15], metal complexes [16, 17] in general and thiazolidinones [18-20] in particular find rare mention in literature. Hence the present investigation is initiated in an effort to probe into the kinetic and mechanistic aspects of cycloaddition reactions of ketoazomethines with thioglycolic acid.

II. MATERIAL AND METHODS

Preparation of ketoazomethines : Phenyl glyoxal (0.2 mol, prepared by partial oxidation of acetophenone with selenium dioxide) and aniline (0.2 mol) were taken in a round bottom flask containing 100 ml of ethanol and refluxed on water bath for 8hrs. Excess of ethanol was removed from reaction mixture and cooled at room temperature. Then it was poured in ice cold water and filtered. Solid obtained was collected and recrystallized with ethanol. Similarly, ketoazomethine of p-diethylaminoaniline was prepared.

Preparation of Solutions : Stock solution of thioglycolic acid (AR, CDH 99.06%) was standardized against standard solution of iodine before use and standard stock solutions of phenyl- and p-diethylamino-anils of phenyl glyoxal were prepared by dissolving known weights of pure products in known volumes of suitable solvents. Stock solution of toluene-4-sulphonic acid (LR, S.D. F.C.L, 98%) was prepared by dissolving its known quantity in known volume. All the kinetic experiments were performed in a thermostatic water bath in ethyl alcohol at different temperatures.

III. RESULTS AND DISCUSSION

The kinetic investigations were performed at different concentration of thioglycolic acid for phenylanil and p-diethylaminoanil, and order of reaction was evaluated. The values of various Arrhenius and Erying parameters were computed from the study of rate measurement within temperature range at 303° – 333° K, respectively.

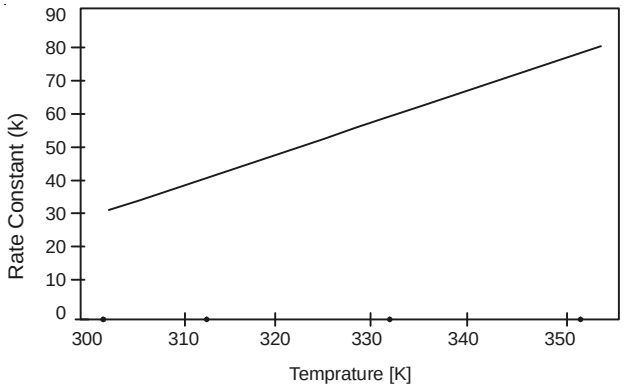

Fig. 1. Plot of rate constant vs. Temp.

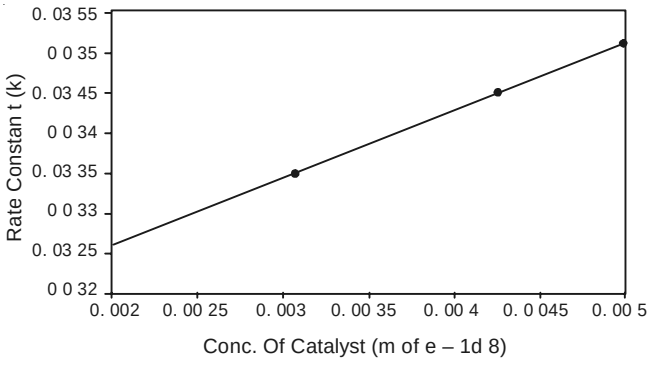

Fig. 2. Plot of rate constant vs. catalyst.

The increase in rate of reaction with increase in concentration of Toluene-4-Sulphonic acid in both cyclocondensation reactions indicates that reactions are acid catalyzed Fig. 2 (Table 3) TSA also acts as dehydrating

agent. Linear plots of 1/ (a-x) vs. time confirm the first order kinetics with respect to both ketoazomethine and thioglycolic acid (Fig.3) and overall second order with respect to both the cyclocondensation reactions. (Tab. 1, 2)

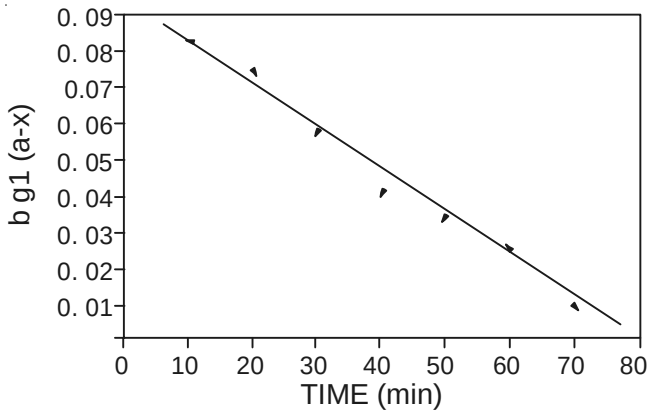

Fig. 3. Plot of time vs. 1/(a-x).

Table 1.

Effect of (Thioglycolic acid) on Rate constant Phenylanil = 0.8 M				Temp. – 298
[Thioglycolic Acid] × 10^3 M	1.230	1.820	2.200	2.654
K_1 × 10^3 min^{-1}	3.076	3.412	3.782	3.197

Table 2.

Effect of (Thioglycolic acid) on Rate constant p-diethylaminoanil = 1 × 10^{-2} M				Temp. –298
[Thioglycolic Acid] × 10^3 M	0.400	0.660	1.000	1.330
K_1 × 10^3 min^{-1}	4.005	4.908	5.234	5.675

Table 3.

Effect of (Catalyst (Toluene 4-Sulphonic Acid) on Rate constant p-diethylaminoanil = 1 × 10^{-2}, Thioglycolic Acid = 1.8 M, [Phenyanil] = 0.8 M				Temp. –298
[TSA]	0.400	0.660	1.000	1.330
K_1 × 10^3 min^{-1}	3.005	6.908	11.234	19.675

The reactions were studied at temperatures 303°, 313°, 323° and 333° K. The lines obtained by plotting k vs. temperature reveal temperature dependence of both the cyclocondensations (Fig. 1). The values of Δ*Ea*, Δ*H**, Δ*S** and Δ*G** and frequency factor (A) for both reactions at different temperatures indicate the slower rate and a rigid transition state in both reactions. (Table 4).

Table 4.

Activation Parameters	**Aniline**	**p-diethylaminoaniline**
Ea(KJ/Mol)	36.23	49.45
A(s^{-1})	2.65	3.56
ΔH* (KJ/Mol)	45.54	58.76
ΔG* (KJ/Mol)	87.80	93.67
ΔS* (J/K Mol)	– 105.67	– 199.43

The Stoichiometry of each reaction under investigation has been determined by equilibrating the reaction mixture containing excess of thioglycolic acid over phenyanil and p-diethylaminoanil, respectively in varying ratio at the experimental temp.At the completion of reaction the unconsumed acid was determined by usual iodometric method. The results of experiments on stoichiometry indicated that the ratio of ketoazomethine and thioglycolic acid was found to be 1:1 for both the reactions.

Values of Δ*H** and Δ*S** are consistent with reaction due to highly organized transition state. The lower value of frequency factor reveals the involvement of similarly charged ions. Higher negative values of Δ*S** at all temperatures for cyclocondensation of p-diethylaminoanil than those obtained in cyclocondensation of phenylanil clearly exhibits direct effect of diethylamino substitution on reaction rate.

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