Kinetics of a Reaction of 3-Chloroacetylacetone with Thioureas

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Abstract

The kinetic study of **3**-chloroacetylacetone and thioureas has been carried out in ethanol. Thioureas used for study are thiourea, phenyl thiourea, p-methyl phenyl thiourea, p-ethoxy phenyl thiourea and p-chlorophenyl thiourea. The second order rate constants for these reaction were reported. The rate of reaction is first order with respect to **3**-chloroacetylacetone and first order with respect to thioureas. The effect of substituents on the rate of reaction was also studied. Thermodynamic parameters are used to explain the nature of the reaction. The reaction products are isolated and characterized. Possible reaction mechanism for the reaction will be proposed and details of the kinetics will be discussed.

Key words: Kinetics, Reaction, 3-Chloroacetylacetone, Thiourea.

Introduction

Thioureas are commercially used in photographic films, plastics and textiles. Thioureas have shown antibacterial, fungicidal[1], hypnotic and antipyretic[2] activities. Some of the thioureas are screened for anticancer activity[3-5]. The use of thiozoles as a vulcanizing accelerators and dye intermediates has been reported[6].

Kinetic and thermodynamic studies on reactions of Pt(II) complexes with pyrozole and 1,2,3 triazole has been carried out[7]. Reaction kinetics of gold dissolution in acid thiourea solution using ferric sulphate as a oxidant was investigated with rotating disk technique[8]. Kinetics and mechanism of reactions between thiourea and iodate in buffer medium has been studied[9]. The kinetics of the reaction of thiourea with formaldehyde was studied[10].

Kinetics of oxidation of thioureas by using various oxidizing agents has been studied[11]. The kinetic study of reactions of thioamides[12] with phenyl bromides is also studied. Kinetics of condensation of allyl/alkyl bromides and allyl thioureas / thioamides[13] has been reported. We have reported kinetic study of reaction of chloroacetone with thioureas[14]. Literature survey reveals that there is no work on kinetic study of reaction of 3-chloroacetylacetone with thioureas.

Experimental Section

3-chloroacetylacetone (Fluka), sodium hydroxide, diethyl ether and phenolphthalein (Qualigens) were used. Aryl thioureas were prepared by Frank and Smith method[15]. Double distilled absolute alcohol was used as solvent to prepare standard solutions of 3-chloroacetylacetone and thioureas. Glass distilled water was used throughout the study.

Kinetic measurements were carried out at different concentrations of reactants and temperatures. A solution containing appropriate amount of thiourea which is thermostated at particular temperature was added in solution containing appropriate amount of 3-chloroacetylacetone at the same temperature. At different time intervals definite volume of aliquot was added to a mixture of diethyl ether and distilled water. It was shaken immediately and the aqueous layer containing thiozole hydrochloride was titrated[16] against standard sodium hydroxide solution using phenolphthalein as an indicator.

Under similar experimental conditions equal amount of thiourea and 3-chloroacetylacetone were mixed and kept overnight. Then reaction mixture was poured on crushed ice. Unreacted reactants were removed by ether extraction. The white solid was crystallized in ethanol and characterized as 2-(substituted amino)–4–methyl–5-acetyl thiozoles on the basis of the reported melting points and their spectral data.

Results and Discussion

The stoichiometric study indicates the one mole of thiourea reacts with one mole of 3-chloroacetylacetone. The rates of reaction were measured at different concentration of thiourea at constant concentration of 3-chloroacetylacetone. The plot of log (dc / dt) against log [thiourea] was straight line and slope of the plot is nearly one. Similarly the rates were determined at different concentration of 3-chloroacetylacetone by keeping concentration of thioureas constant. The plot of log (dc / dt) against log [3-chloroacetylacetone] is also straight line and slope of the plot is nearly one. By using Van't Hoff's differential method[17] the order of reaction with respect to 3-chloroacetylacetone and thioureas was also determined. Second order rate constants were determined at five different temperatures. The energy of activation (Ea) was determined by plotting graph of log k verses 1/T and other thermodynamic parameter were calculated, [Table-1] The entropies of activation (ΔS^*) of these reaction are negative indicates rigid nature of the transition state. The negative value of entropies of activation (ΔS^*) also indicates that less stable noncyclic reactant convert into stable cyclic products. Almost equal values of free energy of activation (ΔF^*) for all thioureas indicates that probably a similar type of mechanism prevails in all cases. When rate constants for the reaction are compared, the thiourea is found to be more reactive than the substituted phenyl thioureas. This may be due to the presence of Л-electron in benzene ring. The phenyl thiourea and p-methyl phenyl thiourea show nearly same rate constants. This may be due to small effect of methyl group due to hyper conjugation and inductive effect. The p-ethoxy phenyl thiourea shows higher rate of reaction due to mesomeric effect.

Table 1: Thermodynamic parameters for reaction of 3-chloroacetylacetone with thioureas

Thioureas	Ea* kJ mol^{-1}	ΔH* kJ mol^{-1}	-ΔS* Jk^{-1} mol^{-1}	ΔF* kJ $mole^{-1}$
Thiourea	42.08	39.48	159.95	89.63
Phenyl thiourea	51.00	48.32	137.87	93.19
p-methyl phenyl thiourea	64.76	62.14	94.61	92.74
p-ethoxy phenyl thiourea	46.25	43.62	153.03	91.60
p-Chlorophenyl thiourea	57.30	53.66	130.74	95.02

The p-chlorophenyl thiourea shows lower rate of reaction due to negative inductive effect of chloro group. In all the reactions 3-chloroacetylacetone is more reactive than chloroacetone[13] as the presence of electron withdrawing group stabilizes enol intermediate in the formation of thiozole.

It is found that, the reaction is second order, first order with respect to thiourea and first order with respect to 3-chloroacetylacetone. The rate constants calculated from second order rate law are fairly constant [Table 2].

Table 2: Second order rate constants for reaction of 3-chloroacetylacetone with thioureas. Thiourea = 0.05 mol dm^3 Temp = 313 ^0K

Thioureas	10^3 dm^3 mol^{-1} s^{-1} at 3-chloroacetylacetone mol dm^{-3}			
	0.05	0.04	0.03	0.02
Thiourea	6.68	6.65	6.70	6.66
Phenyl thiourea	2.73	2.77	2.70	2.76
p-Totyl thiourea	3.31	3.28	3.35	3.36
p-Phenitidinyl thiourea	3.18	3.25	3.15	3.19
p-Chlorophenyl thiourea	1.42	1.39	1.44	1.40

Based on these facts, the following general mechanism and rate expression is proposed.

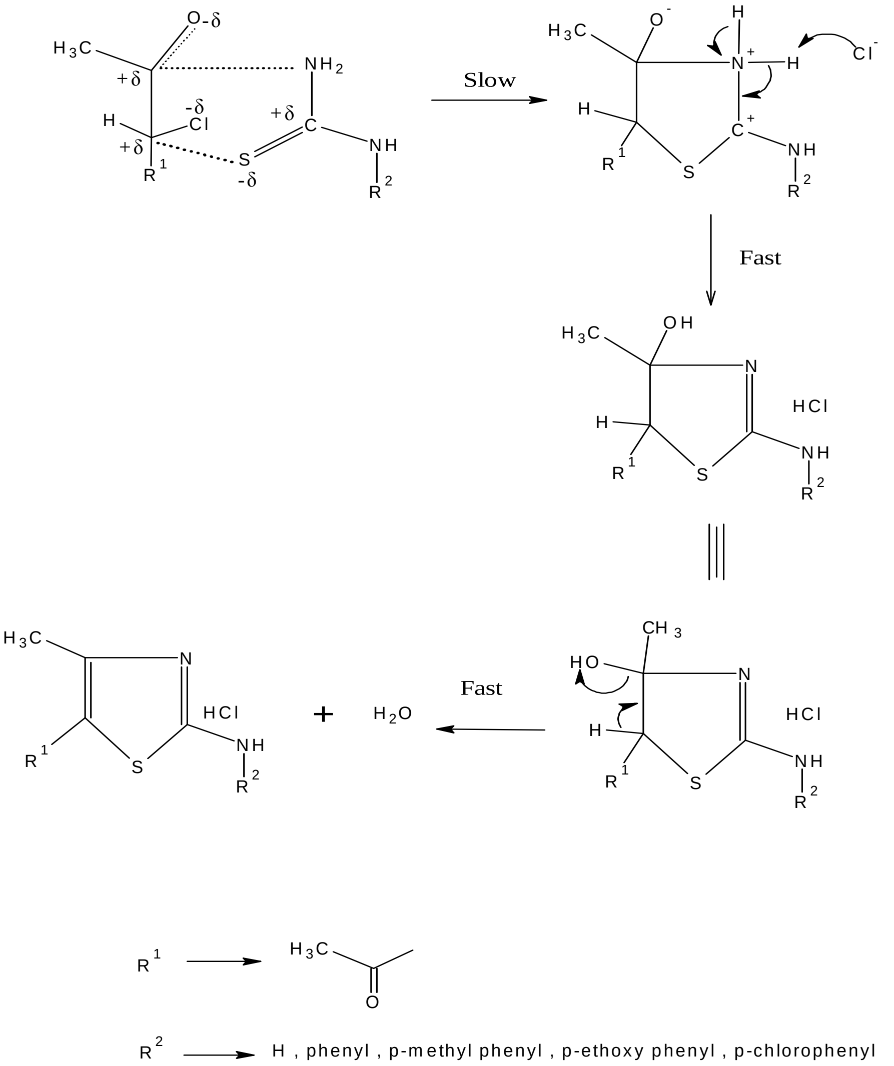
$$S_1 + S_2 \underset{k_{-1}}{\overset{k_1\ \text{Slow}}{\rightleftharpoons}} [\text{ Intermediate }] \xrightarrow[k_2]{\text{Fast}} \text{products ---- (1)}$$

S_1 stands for **3**-chloroacetylacetone and S_2 stands for thioureas.
Rate of reaction = $k_1 [S_1] [S_2] - k_{-1} [\text{Intermediate}]$ ---------- (2)

On applying steady state approximation.

$$d / dt\,[\text{ Intermediate }] = o = k_1\,[\,S_1\,]\;[\,S_2\,] - k\text{-}_1\,[\text{ Intermediate }] - k_2\,[\text{ Intermediate}] \text{ ------ } (3)$$

$$[\text{Intermediate}] \quad = \quad \frac{k_1\,[\,S_1\,]\,[\,S_2\,]}{k_{-1}\ +k_1} \qquad \text{----------------- } (4)$$



Scheme I

Substituting the value of [Intermediate] in equation (2)

$$\text{Rate of reaction} = k_1 [S_1] [S_2] - \frac{k_{-1} k_1 [S_1] [S_2]}{k_{-1} + k_2} \quad \text{------} \ (5)$$

$$\text{Rate of reaction} = \left\{ k_{-1} - \frac{K_{-1} k_1}{K_{-1} + k_2} \right\} [S_1] [S_2] \quad \text{----------} \quad (6)$$

$$\text{If} \quad k' = \left\{ k_{-1} - \frac{k_{-1} k_1}{k_{-1} + k_2} \right\}$$

Rate of reaction = $K' [S_1] [S_2]$

The order of reaction is two. The derived rate law explains all the observed experimental facts.

Conclusion

- The rate of reaction between 3-chloroacetylacetone and thiourea is found to be two.
- The proposed rate law also shows that the rate of reaction is two.
- Nearly equal values of free energy (ΔF^*) indicates that same type of reaction mechanism prevails.
- Decrease in entropy (ΔS^*) indicates that from open chain compound cyclic compounds are formed.

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