Kinetics and Mechanism of Oxidation of Alizarin Red-S Using Chloramine-T in Acid Medium

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Abstract-- Kinetics of the oxidation of 1,2 dihydroxyanthraquinone, mordant vegetable dye (ALZ) byN-chloro-p-toluenesulfonoamide (CAT) in per chloric acid medium at 28°C was studied spectrophotometrically. The reaction showed first order dependence on both [substrate] and [oxidant]. The reaction failed to initiate the polymerization of added acrylonitrile and this erase the involvement of radical intermediate in the reaction. A mechanism is proposed to account for the kinetic data obtained. The method adopted for the oxidation of mordant dye in the present work offers several advantages and can be scaled up to dye industries and for various dye fabrication processes.

Key words-- *Kinetics of oxidation, Alizarin, Chloramine-T*

I. INTRODUCTION

Alizarin or 1, 2-dihydroxyanthraquinone also known as Mordant red and Turkey Red[1] is an organic compound with molecular formula $C_{14}H_8O_4$ that has been historically used as an prominent dye mainly for dyeing textile fabrics. Naturally, it is derived from the roots of madder genus [2] plants.

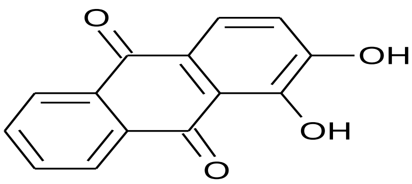


Figure 1: Structure of Alizarin (Molecular mass: 364.24)

Alizarin (madder) has been used in textile dyeing since early antiquity. And it is the first dye which has been synthesized in laboratory and is now finding usage in painting industry. Alizarin is used in medical studies in bone growth, bone marrow, osteoporosis, tissue engineering and also in geological studies in the determination of calcium content.

A method for the synthesis of alizarin was first discovered (1868) by Karl Graebe and Karl Liebermann, German chemists.(λ_{max}=525nm) With salts of metals, the compound forms brilliant lakes, although by itself it is a poor dye. Turkey red is produced with an aluminum mordant, other shades of red with calcium and tin salts, dark violet with iron mordants, and brownish red with chromium. Purpurin, also used in dyeing, occurs with alizarin in madder and is produced synthetically.

The oxidant selected in our oxidation study is Chloramine-T. Considerable attention has centered around the chemistry of N-metallo-N-arylhalosulphonamides, generally known as organic haloamines, because of their versatility, and their behavior as an oxidizing agent in both acidic and alkaline media [3]. It is an important oxidizing agent and has shown a variety of kinetic results due to formation of its various oxidizing species depending upon pH of the medium[4-8].Generally, CAT undergoes a two-electron change in its reactions resulting in the formation of the reaction product, p-toluenesulphonamide or PTS (p-$CH_3C_6H_4SO_2NH_2$) and sodium chloride. A detailed review of the chemistry of CAT and related N-haloarylsulfonamides has been reported [9]. It can behave as both electrophiles and nucleophiles depending on reaction conditions [10].

Chloramine-T (CAT), a by-product in saccharin manufacture, is well-known as an analytical reagent, and the mechanistic aspects of its reactions have been well-documented [11-13].

II. EXPERIMENTAL

A. Materials and Methods

All the reagents were of analytical reagent grade and all the solutions were prepared in doubly distilled water and CO_2 free deionized water. A solution of alizarin, 10x10^{-3}mol/$dm^3$was prepared by dissolving 0.3642g of alizarin in water, and the solution was diluted to the mark in100cm^3 volumetric flask. Chloramine-T was prepared [14] by passing chlorine through a solution of benzenesulphonamide in 4mol/dm^3 NaOH for an hour. The product was collected, dried and recrystallized from water (m.p. 167°C). Its purity was checked by iodometry for its active chlorine content and also by its ^{1}H and ^{13}C-NMR spectra. An aqueous solution of CAT was standardized iodometrically. Both the solutions of Alizarin and CAT were stored in dark glass bottles to prevent the photochemicaldeterioration of the reagents. Perchloric acid (E. Merck) was prepared in double distilled water, without any further purification. Absorbance was recorded on UV-VIS Spectrophotometer at wavelength525nm[15].

B. Kinetic measurements

In the present study, the kinetics of the reaction was carried out at room temperature 25°C. Kinetic runs were performed under pseudo first-order conditions with a known excess of $[CAT]_o$ over $[ALZ]_o$. The kinetics of oxidation of Alizarin by CAT was investigated at several initial concentrations of the reactants in acid media.The reaction was initiated by mixing the ALZ to CAT solution, which has been diluted to a constant volume, and the progress of the reaction was followed spectrophotometrically at 525nm by monitoring the decrease in absorbance due to CAT.

The pseudo first order rate constant, 'k_{obs}' were determined from log (Do/Dt) vs time plots. The plots were linear up to 85% completion of reaction under the neutral media. The orders for various species were determined from slopes of plots of logk_{obs} vs respective concentration of species.

III. RESULTS AND DISCUSSION

3.1 The figure (1) shows the plot of log(Do/Dt) Vs time at 297K. The observed rate k_{obs} were calculated from the slopes of the straight lines by linear regression. The electron transfer reaction between [ALZ] and [CAT] has been studied over the range of 5x10^{-4} to 25x10^{-4} and 1.25 x10^{-3} to 7.5x 10^{-3}mol/dm^3 respectively. The observed rate constant, log k_{obs} were plotted against log concentration.The values of pseudo first-order rate constants, k' remained unaltered with variation of log$[ALZ]_o$ confirming the first-order dependence on [ALZ].

Plots of logk' Vs log[CAT] whose(r= 0.9435) with unit slope showing first-order dependence on the rate of [CAT].

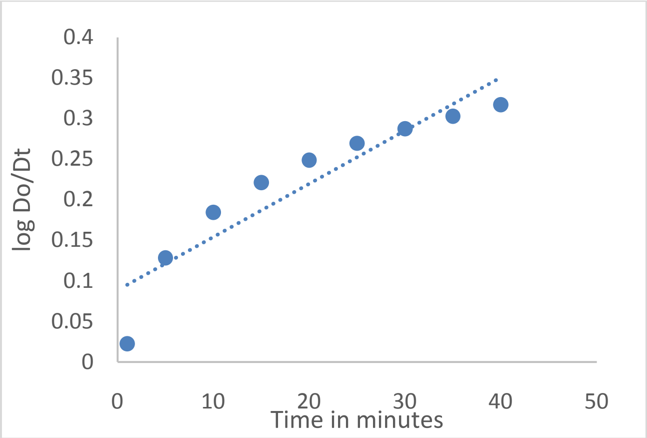


Figure 2: Plot of log(Do/Dt) Vs time in minutes.

2.2 Effect of variation of Alizarin concentration. The concentration of alizarin was varied from $5x10^{-4}$ to $25x10^{-4}$ mol/dm^3 at fixed concentration of other reactants. A plot of initial rates Vs [ALZ] showed first-order dependence with the reductant(Figure: 2). The constant value of k(Table: 1) indicate the unit order with respect to Alizarin.

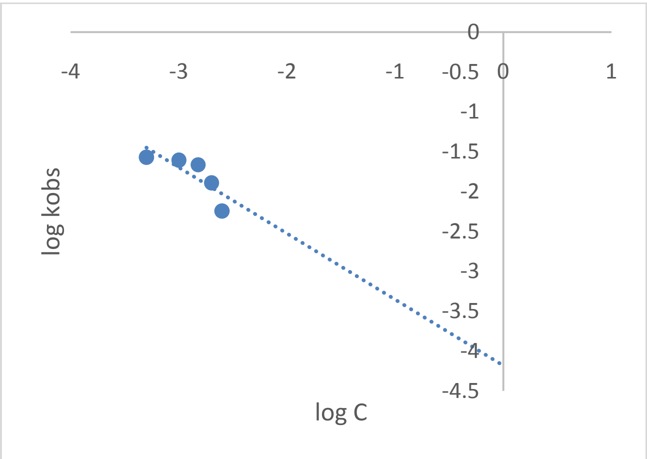


Figure 3: Graph to study the variation of reductant on the reaction rate

2.2 Effect of variation of CAT concentration. The concentration of CAT was varied from 1.25 $x10^{-3}$ to 7.5x 10^{-3} mol/dm^{-3}at fixed concentration of other reactants. A plot of initial rates versus concentration of CAT shows a unit order dependence with oxidant.(Figure: 3)

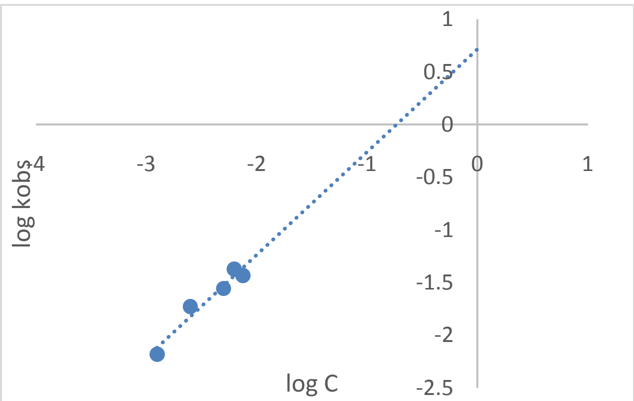


Figure 4: Graph to study the variation of oxidant on the reaction rate.

Table: 1

$[ALZ]x10^{-4}$ mol/dm^{-3}	$[CAT]x10^{-3}$ mol/d m^{-3}	k_{obs}
5	5	0.0270
10	5	0.0248
15	5	0.0217
20	5	0.0129
25	5	0.0057
5	1.25	0.0066
5	2.5	0.0187
5	5	0.0277
5	6.25	0.0423
5	7.5	0.0367

Chloramine-T acts as an oxidizing agent in both acidic and alkaline medium. It undergoes a two-electron change in its reactions. As said, the reduction potential of CAT is pH dependent [16] and decreases with an increase in pH of the medium. Depending on the pH of the medium, CAT furnishes different types of reactive species in the solution. [17-19]

$$TsNClNa \rightleftharpoons TsNCl^- + Na^+$$

$$TsNCl^- + H^+ \rightleftharpoons TsNHCl$$

$$2TsNHCl \rightleftharpoons TsNH_2 + TsNCl_2$$

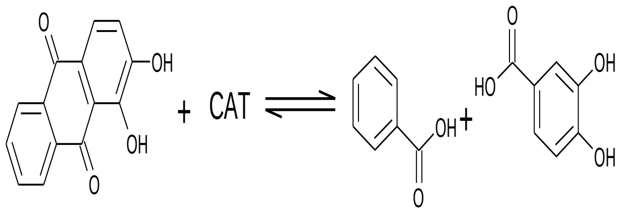
$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl$$

$$TsNCl_2 + H_2O \rightleftharpoons TsNHCl + HOCl$$

$$HOCl \rightleftharpoons H^+ + OCl^-$$

$$HOCl + H^+ \rightleftharpoons H_2O^+Cl$$

Therefore, the probable reactive species in acid solution of CAT are TsNHCl, $TsNCl_2$, HOCl and H_2O^+Cl. Under the present experimental conditions, the effective oxidizing species may be TsNHCl.



CONCLUSION

Development in science and technology leads to vast growth of industries and factories. Many industries use dyes for various purposes like pigmentation, colouring products. Paper, food, cosmetics and textile industrial unit frequently produce coloured residual effluents, which are undergone treatment before passing into water sources. The presence of dyes and industrial dyestuffs in water even in ppm level causes disturbance for aquatic life. The present redox system can be adopted for treating Alizarin dye present in industrial effluents with suitable modifications to reduce the toxicity caused by alizarin through decoloration. The study could also be used in medical and geological studies.

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