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OXIDATION KINETICS OF ANILINE BY ZINC DICHROMATE

M. Subathra, M. Vellaisamy*

Department of Chemistry, KunthavaiNaachiyaar Government Arts College for Women,
(Affiliated to Bharathidasan University) Thanjavur, Tamil Nadu, India
**Corresponding author: prof.m.vellaisamy@gmail.com*

ABSTRACT

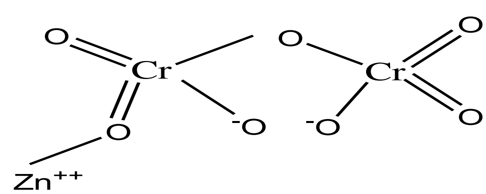
The kinetics of oxidation of aniline by Zinc Dichromate (ZDC) has been studied in 50% acetic acid-water medium. The reaction shows unit order dependence each with respect to oxidant and substrate. The rate of reaction increases with increase in the [H^+]. The rate of oxidation increases with decrease in dielectric constant of solvent suggests ion-dipole interaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate constant. There is no polymerization with acrylonitrile and absence of free radical is proved. The rate of the reaction has been conducted at four different temperatures. Thermodynamic parameters have been calculated. Based on the kinetics results, a suitable mechanism has been proposed.

Keywords: Zinc Dichromate, Aniline, Kinetics, Oxidation, Mechanism.

1. INTRODUCTION

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds [1]. Chromium especially, Cr (VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidizable organic functional groups [2, 3]. Zinc Dichromate (ZDC) is also one of the important oxidizing reagent [4]. Zinc Dichromate has the following advantages over already reported Cr (VI) reagents: (i) quite stable at room temperature (ii) not photosensitive (iii) less hygroscopic and hence a suitable reagent for the oxidation of acid sensitive and ring strained alcoholic as readily soluble in acetic acid. Anilines (aromatic amines) are the most widespread and principal contaminants of industrial waste water. This consists of environmental contaminants and they are the building blocks for many textile dyes, agro chemicals and other type of synthetic chemicals. The reaction pathways of aromatic amines in natural systems are dominated by redox reaction with soil and sediment constituents. Better understanding of the mechanism of oxidation of such contaminants to harmless products is the important goal for basic research and industrial applications. Hence, in the presence study, kinetics of oxidation of anilines by Zinc Dichromate is carried out.

Zinc dichromate (ZDC) is a red crystalline compound. It is a chromium (VI) oxidant. It is used as a mild oxidant of different classes of compound. The formula of zinc dichromate is $ZnCr_2 O_7 . 3H_2O$.



2. EXPERIMENTAL

2.1. Material and Methods

Aniline was distilled and purified. Zinc Dichromate was prepared by reported method [4], and its melting point was checked (285°C). Acetic acid was purified by standard method [5] and the fraction distilling at 118°C was collected and saved in brown bottles. All other chemicals used were of AnalaR grade. The solutions were prepared in double distilled water.

2.2. Preparation of Zinc Dichromate [5]

To a cold solution of chromic acid (2.36 g) prepared by addition of chromium trioxide (2.00g) to a 3.4 molar solution of sulfuric acid (6ml), Zinc corbanate (1.25 g) was added in portions within 15 minutes. A dark reddish solution was produced by the evaporation of the solvent under vacuum affords an orange red slurry which is completely dried on the surface of a highly dried on the surface of a highly dried clay plate in the air; Yield (2.68 g) 80%.

2.3. Kinetic Measurements

The kinetic studies were carried out under pseudo-first order conditions in 50% *(v/v)* aqueous acetic acid with the concentration of the aniline in large excess compared to that of the oxidant. All reactant solutions were placed in a thermostated water bath for one hour to attain the temperature of 30°C. Appropriate quantities of the reagent solutions were mixed in a 250 cm^3 conical flask already placed in the thermostated bath. The reaction rate was followed by measuring the decrease in absorbance at 470nm for up to 80% completion of the reaction by using systronics UV-vis spectrophotometer. The reactions were followed determining the concentration of the unreacted ZDC, at known intervals of time. The pseudo-first order rate constants k_1 computed from the linear plots of log absorbance *versus* time by the least squares method were reproducible within ±1% .

2.4. Stoichiometry

The stoichiometry of the reaction was determined by carrying out several set of experiments with varying amounts of ZDC in large excess over aniline. The estimation of the unreacted oxidant showed that one mole of aniline consumed one mole of the oxidant.

2.5. Product analysis

To the substrate (0.1mole) in acetic acid, ZDC (0.1mole) in water was added and the medium was maintained in acetic acid using perchloric acid the reaction mixture was then slightly warmed and was kept aside for about 48 hr for the completion of reaction. After 48 hr, the reaction mixture was extracted with ether and dried over anhydrous sodium sulphate. The ether layer was washed with water several time and kept on a water bath for ether evaporation and cooled to get the product. The azobenzene formed as the product of oxidation under kinetic condition was confirmed by TLC, IR as well as GC-MS spectra.

3. RESULTS AND DISCUSSION

Oxidation of aniline by Zinc Dichromate was conducted in 50% acetic acid - 50% water *(v/v)* medium at 303 K under pseudo-first order condition and the observed results are discussed in respective sections.

3.1. Effect of varying [ZDC]

The reaction was investigated with varying concentration of Zinc Dichromate at constant aniline and perchloric acid concentration. The reaction was found to be first order with respect to [ZDC] as evidenced by the liner plot of log absorbance *versus* time and also from the constancy of the pseudo- first order rate constant as shown in table 1.

3.2. Effect of varying [Substrate]

The reactions were carried out at 303 K with varying the concentration of aniline while keeping the concentration of all other factors constant. The rate constant k_1 increased with increase in substrate concentration. The plot of log k_1 *versus* log [substrate] (Fig. 1) gave a straight line with a slope of 1.0 (r=0.99) and shows that oxidation reaction was first order with respect to [aniline]. This was further demonstrated by the constancy of the specific reaction rate $k_2 = k_1/[s]$.

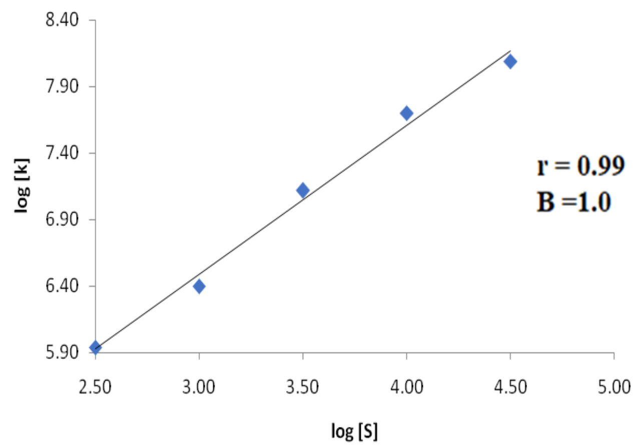


Fig. 1: plot of log k_1 *versus* log [substrate]

3.3. Effect of varying [H^+]

The reaction was followed with different concentrations of hydrogen ion while other variables were kept constant. The rate of the reaction increases with slight increase in the hydrogen ion.

3.4. Effect of solvent composition

The reaction rate was measured of different acetic acid-water mixtures, while all other factors were kept constant. It was observed that an increase in the percentage of acetic acid increases the rate of the reaction.

3.5. Effect of added Acrylonitrile

The clear reaction mixture containing Aniline and Zinc dichromate was allowed to stand with a drop of acrylonitrile, no turbidity was formed showing the absence of free radical pathway.

Table 1: Rate data for Oxidation of Aniline by Zinc Dichromateat 303K

[Oxidant] 10^3*mol dm*$^{-3}$	[Substrate] 10^2*mol dm*$^{-3}$	[$HClO_4$] 10^2*mol dm*$^{-3}$	%CH_3COOH-%H_2O (% v/v)	[$AlCl_3$] 10^2*mol dm*$^{-3}$	k_{obs} 10^4 s^{-1}
2.0	2.5	1.0	50-50	-	5.94
2.5	2.5	1.0	50-50	-	5.93
3.0	2.5	1.0	50-50	-	5.01
3.5	2.5	1.0	50-50	-	5.12
2.0	2.5	1.0	50-50	-	5.94
2.0	3.0	1.0	50-50	-	6.19
2.0	3.5	1.0	50-50	-	7.12
2.0	4.0	1.0	50-50	-	7.99
2.0	4.5	1.0	50-50	-	8.02
2.0	2.5	1.0	50-50	-	5.94
2.0	2.5	1.5	50-50	-	6.24
2.0	2.5	2.0	50-50	-	6.28
2.0	2.5	2.5	50-50	-	6.76
2.0	2.5	3.0	50-50	-	7.21
2.0	2.5	1.0	50-50	-	5.94
2.0	2.5	1.0	55-45	-	6.21
2.0	2.5	1.0	60-40	-	6.76
2.0	2.5	1.0	65-35	-	7.15
2.0	2.5	1.0	70-40	-	7.49
2.0	2.5	1.0	50-50	0.0	5.94
2.0	2.5	1.0	50-50	2.5	4.90
2.0	2.5	1.0	50-50	3.0	4.10
2.0	2.5	1.0	50-50	3.5	3.50
2.0	2.5	1.0	50-50	4.0	2.90

3.6. Effect of Aluminium chloride

In order to know whether the reaction follows three electron transfer process, the rate of reaction was followed with various initial concentrations of $AlCl_3$ at constant [substrate], [oxidant], [$HClO_4$], and temperature. A considerable rate decrease is observed which can be taken as evidence for three electron transfer process.

3.7. Effect of varying the temperature

The reaction has been studied at four temperatures such as 303, 308, 313and 318 K while keeping all the other factors constant. The rate of reaction increases with increasing temperature. The following thermodynamic parameters have been computed from the linear plot of ln (k_2/T *versus* 1/T) (r = 0.99) of the Eyring'sequation [6] (Fig 2) and it was found to be linear [7].

Temperature (K)	k_1 10^4 s^{-1}	Activation parameters
303	5.94	$\Delta H^{\#} = 29.25$ *kJmol*$^{-1}$
308	6.21	$\Delta S^{\#}$ =-179.89*JKmol*$^{-1}$
313	6.76	$\Delta G^{\#}$= 93.86*kJ mol*$^{-1}$at 303 K
318	7.15	E_a = 31.76*kJ mol*$^{-1}$at 303 K

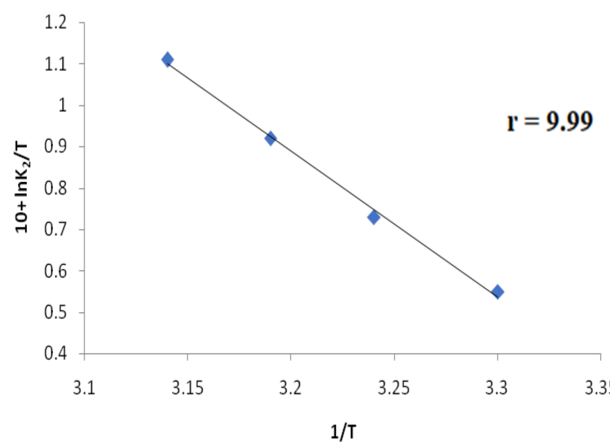
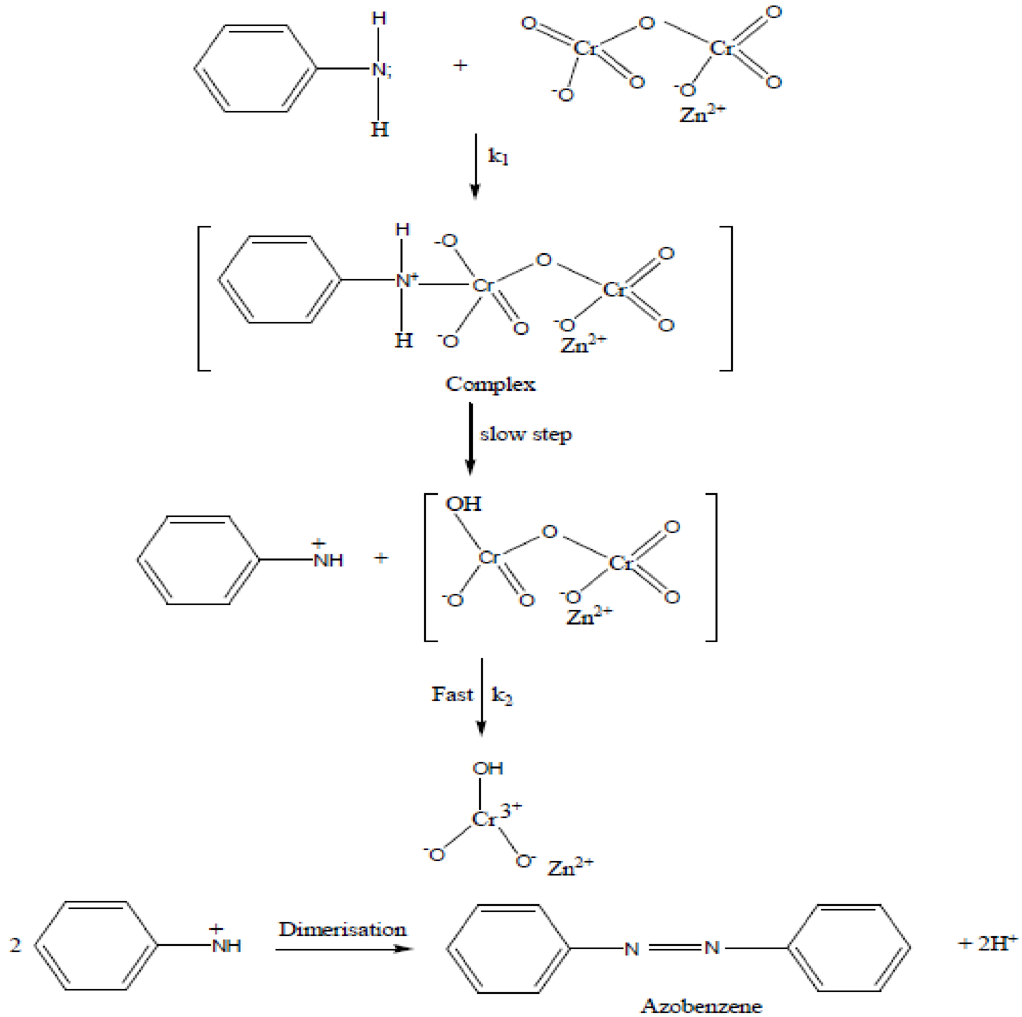


Fig. 2: plot of lnk_2/T *versus* 1/T

3.8. Mechanism and Rate Law

The mechanism of reaction for the oxidation of aniline by zinc dichromate in an acid medium is shown in scheme 1. The reaction is showing unit order dependence with respect to oxidant and substrate. The oxidant and substrate gives complex. The complex undergoes dimerization and gives azobenzene as product.



Rate law

$$-d\,[ZDC] = k_1k_2[ZDC][Aniline]$$

4. CONCLUSION

The kinetics of oxidation of aniline has been investigated in aqueous acetic acid medium spectrophotometrically. The reaction shows unit order dependence each with respect to oxidant and substrate. The lowering dielectric constant of reaction medium increases the reaction rate significantly. The reaction does not form the polymerization which indicates the absence of free radical intermediate in the oxidation reaction. The oxidation of aniline yielded the corresponding azobenzene.

5. ACKNOWLEDGEMENT

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Conflict of interest

None declared

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