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Research Article

Kinetics of Oxidation of Oxine by Isoquinolinium Bromochromate

M.Vellaisamy* and M.Hinduja

Department of Chemistry, Rajah Serfoji Government College,(Autonomous) Thanjavur, Tamilnadu,India

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Abstract: The kinetics of 8-hydroxy quinoline (oxine) by isoquinolinium bromochromate has been studied in 50% acetic acid-water (v/v) medium. The order of the reaction has been found to be one with respect to oxidant, second order with respect to substrate and zero order with respect to hydrogen ion concentration. Decreases in dielectric constant of the medium, increases the rate of the reaction.Increases in ionic strength has no effect on the reaction rate. The reaction does not induce the polymerization of acrylonitrile. Quinoline-5, 8-quinone has been identified as a product. From the kinetic data obtained, the activation parameters have been calculated and a possible mechanism has been proposed.

Keywords: Kinetics, oxidation, isoquinolinium bromochromate, 8 hydroxyquinoline (oxine), activation parameter.

INTRODUCTION

Halo Chromates have been used as mild and selective oxidizing reagent in synthetic organic chemistry. A variety of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group. The kinetics and mechanism of oxidation of Cr (VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with diverse substrates. The development of newer chromium (VI) reagents for the oxidation of organic substrates continues to be of interest.

A number of new chromium containing compounds like pyridinum bromochromate[1], quinolinium chlorochromate[2], 2 – bipyridinium chlorochromate[3], pyridiniumfluoro chromate[4], quinolinium fluorochromate[5], quinolinium bromochromate[6], quinolinium dichromate[7], pyridinium fluorochromate[8],

imadazoliumfluorochromate[9] have been used to study the kinetics and mechanism of oxidation of various organic compounds.

However, most of the reagents developed so far suffer from at least one of the drawbacks such as high acidity, photo sensitivity, instability, hygroscopicity, low selectivity, long reaction time and need for large excess of reagent. To overcome these disadvantages, we have used isoquinoliniumbromo chromate (IQBC) as a new mild efficient and stable reagent, which is able to work as an oxidizing agent.

The oxidation of the reactive substrate, oxine, has been studied extensively with N – chloro – 3 – methyl-2, 6 – diphenylpiperidin – 4 – one, a mild and selective oxidant[10] and oxidation of Oxine by Isoquinolinium dichromate has also been studied[11]. Literature survery reveals that no report is available on the kinetics of oxidation of oxine by isoquinolinium bromochromate(IQBC). Hence, we have considered it worthwhile to study the kinetics of oxidation of oxine by IQBC.

EXPERIMENTAL

All the chemicals and reagents were of analytical grade. E. Merck Isoquinolinium bromochromate was prepared by reported method[12]. 8-hydroxyquinoline was purified by repeated recrystallization in ethanol to constant melting point (75-76℃). All the other chemicals used were of AnalaR Grade. The reaction was carried out under pseudo – first order conditions [oxine]>> IQBC] in 50% aqueous acetic acid containing perchloric acid. The course of the reaction was allowed colorimeter at 470nm for up to 80% of the reaction. The pseudo – first order rate constants k, computed from the linear plots of log absorbance versus time by the least squares method, were reproducible with in ± 2%.

RESULTS AND DISCUSSION

Oxidation of oxine by isoquinolinium bromochromate has been conducted in 50% acetic acid and 50% water medium at 303 k under pseudo – first order conditions and the observed results were discussed.

The order of the reaction with respect to Isoquinolinium bromochromate was found to be unity as shown by the linearity of log absorbance against time plots, above 80% of the reaction. The reaction was found to be second order in [substrate] as evidenced by the slope (2.0) of the plotof $\log k_1$ against log [substrate] **Table-1.**

Table-1: Rate Constant for the oxidation of oxine by IQBC at 303k

[Oxine] x 10^2 mol dm^{-3}	[IQBC] x 10^3 mol dm^{-3}	[$HClO_4$] x 10^2 mol dm^{-3}	[$NaClO_4$] x 10^4 mol dm^{-3}	[ACOH-H_2O] (%v/v)	[$AlCl_3$] x 10^4 mol dm^{-3}	K_{obs} x 10^4 S^{-1}
3.5 - 5	1.5	2.0	-	50	-	3.29 – 6.77
3.5	1.5-3.0	2.0	-	50	-	3.29 – 3.08
3.5	1.5	2.0– 3.5	-	50	-	3.29 – 3.04
3.5	1.5	2.0	0-10.0	50	-	3.29 – 3.78
3.5	1.5	2.0	-	50-65	-	3.29 – 5.69
3.5	1.5	2.0	-	50	0-7.5	3.29 – 1.99

The reaction was followed with different concentrations of perchloric acid and keeping all the concentrations as constant and rate were measured **(Table-1).** The rate constants were constant by the

addition of H^+ ion during the reaction. Hence, the rate of the reaction is independent of hydrogen ion concentration.

The effect of solvent composition on the reaction rate was studied by varying the concentration of acetic acid 50% - 65%. The reaction rate increases with increase in the proportion of acetic acid in the medium (Table.1). When the acetic acid content increases in the medium the acidity of the medium is increased whereas the dielectric constant of the medium is decreased suggesting ion - dipole interaction.[13,14] The clear mixture containing oxine and IQBC other allowed to stand with a drop of acrylonitrile[15]. No turbidity is formed suggesting the non-involvement as free radicals in this reaction.

To have an idea about the number of electron involved in the oxidation process. The added Mn^{2+} ions have a noticeable catalytic effect on the reaction rate. As the concentration of aluminium chloride was increased, the rate of the reaction was decreased it is evident for the three electron transfer process in this reaction.

The rate constants were measured at four different temperatures and the activation parameters have been calculated from the linear Eyring's plot as ln (K_2/T) against 1/T by the least squares method.[16] **(Table-2)**

$\Delta H^{\#} = 36.197$ kJmol^{-1}

$\Delta S^{\#} = -267.1810$JK^{-1} mol^{-1}

$\Delta G^{\#} = 118.47166$ kJ mol^{-1} at 303k

E a = 38.7176kJ mol^{-1} at 303k

Table 2 Activation Parameters for the oxidation of oxine by Isoquinoliniumbromo chromate

[IQBC] = 1.5 x 10^{-3}mol dm^{-3} [$HClO_4$] = 2.0 x 10^{-2}mol dm^{-3}

[oxine] = 3.5x 10^{-2}mol dm^{-3} 50% Acetic acid 50% water medium

S. No	Substrate	104 kobs s-1				ΔH# (kJmol-1)	-ΔS# (JK-1 mol-1)	ΔG# (kJmol-1) at 303 K	Ea (kJmol-1) at 303 K
		303K	308K	313K	318K				
1	oxine	3.29	4.69	5.71	6.88	36.19	267.18	118.47	38.71

Stoichiometry and product analysis: The reaction mixture containing an excess of oxidant over oxine were kept at room temperature in the presence of perchloric acid for 24hour. Estimation of the unchanged oxidant showed that one mole of oxidant consumed two mole of the substrate. The overall stoichiometry of the reaction is 1:2.

The product, quinoline-5,8-quinone, was identified by spot test and IR, UV spectra[17] GC-MS spectra.

Mechanism and rate law: From the above observation, it is clear that the reaction is slowing first order dependence on oxidant and second order dependence on substrate. The concentrations of the total Cr (VI) and dimer are not differing too much.

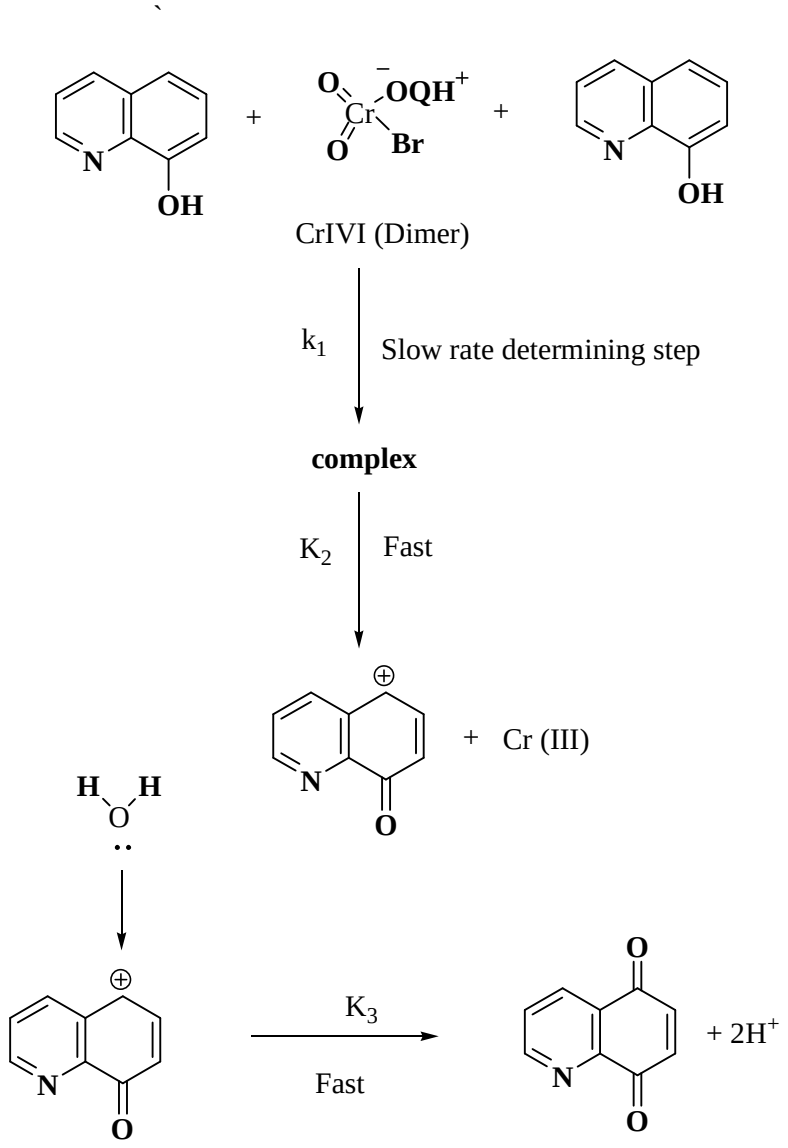
The reaction is not catalyzing by the acid and the rate remains constant with the increase of hydrogen concentration. The ionic strength of the medium shows a negligible effect on the rate of the reaction. The rate of the reaction increases with the decreasing the dielectric constant of the medium. Based on the

above facts, the following mechanism has been proposed for the oxidation of oxine by isoquinoliniumbromo chromate. (**Scheme – 1**)

The rate law:

The above mechanism is to the following rate law

Rate = k_1 [IQBC] [oxine]



Scheme -1

$$-\frac{d[IQBC]}{dt} = k_1 [IQBC][oxine]^2$$

$$-\frac{d[IQBC]}{dt} = k_{obs} [IQBC][oxine]^2$$

This rate law explains all the observed experimental facts.

CONCLUSIONS

The oxidation of oxine by IQBC in aqueous acetic acid medium leads to the formation of a complex giving quinoline – 5, 8 – quinone as the final product. The reaction follows simple order kinetics reaction. The mechanism proposed for this oxidation kinetics is based on the observed kinetic facts.

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Corresponding author: M.Vellaisamy; Department of Chemistry,
Rajah Serfoji Government College,(Autonomous) Thanjavur, Tamilnadu,India