Kinetics and mechanism of Mn(II) catalyzed oxidation of acridine yellow by chloramine-T

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The kinetics and mechanism of the uncatalyzed and Mn(II) catalyzed oxidation of acridine yellow (3,6-diamino-2,7-dimethyl acridine hydrochloride) dye by chloramine-T in acidic media has been studied using spectrophotometry. With excess concentrations of other reactants, the reaction rate follows pseudo first order kinetics with respect to acridine yellow. The uncatalyzed reaction has fractional order dependence on chloramine-T as well as on H\textsuperscript{+} concentration. The catalyzed reaction follows first order kinetics in catalyst [Mn(II)]. Variations of ionic strength has no influence on the reaction rate suggesting that neutral charge d species are in catalyst [Mn(II)].

The basic stoichiometric equation is as follows: AY\textsuperscript{+} + ArSO\textsubscript{2}NClNa.1.5H\textsubscript{2}O, CAT) is a widely studied oxidant\textsuperscript{12,13}. We report herein the detailed kinetics of both the uncatalyzed and Mn(II) catalyzed reactions of chloramine-T with acridine yellow and have proposed mechanisms based on the results obtained.

Experimental

All chemicals used were of Analar grade and doubly distilled water was used throughout to prepare the solutions. An aqueous solution of chloramine-T (Merck) was prepared and standardized periodically by the iodometric method and preserved in an amber-coloured bottle until further use. The aqueous solution of AY\textsuperscript{+} (Aldrich) was prepared by dissolving 0.0274 g of AY\textsuperscript{+} in 100 cm\textsuperscript{3} of water. Working solutions were prepared by appropriate dilution of the stock solution. The stock solution of Mn(II) was prepared by dissolving 0.0169 g of Mn(II) sulphate (Aldrich) in 100 cm\textsuperscript{3} of water\textsuperscript{14}. Stock solution of H\textsubscript{2}SO\textsubscript{4} was prepared by diluting the calculated volume (from density) of acid with distilled water and finally its concentration was determined by titrating it against standard NaOH solution using phenolphthalein as indicator.

Kinetic procedure

In all experiments, the pseudo-first order kinetics with respect to acridine yellow was monitored at 445 nm, using systronix UV-vis spectrophotometer. No interference from other reagents, intermediates or oxidizing states of Mn(II). Although many complexes of Mn(II) with various organic and inorganic substances have been reported\textsuperscript{3,5}, literature survey shows few kinetic investigations on the oxidation reactions of dyes in general acridine yellow dye in particular involving Mn(II) as a homogeneous catalyst. Acridine yellow dye is used for dying leather, paper, lacquer and in spirit inks\textsuperscript{6}. Due to its stability, it has long residence time in water and is hazardous in the aquatic system\textsuperscript{7,8}. Thus, the color removal process and the degradation dynamics of the dye are of urgent need. Literature survey reveals that oxidation of different dyes by various oxidants has been studied\textsuperscript{9-11}, but no information is available on the oxidative degradation of the acridine class dyes by chloramine-T. Chloramine-T (p-Me-C\textsubscript{6}H\textsubscript{4}-SO\textsubscript{2}NClNa.1.5H\textsubscript{2}O, CAT) is a widely studied oxidant\textsuperscript{12,13}. We report herein the detailed kinetics of both the uncatalyzed and Mn(II) catalyzed reactions of chloramine-T with acridine yellow and have proposed mechanisms based on the results obtained.
product was observed at 445 nm. Beer's law was valid, under the experimental conditions considered herein. The total initial volume of the reaction mixture was always kept 10 ml and at (25±0.1)°C. Reagent solutions were mixed in the order: acridine yellow, sulphuric acid, plus catalyst and water or other reagents where necessary in the required volumes. Separately, thermally equilibrated solution of chloramine-T was added to commence the reaction. After vigorous mixing, the solution was transferred to the spectrophotometer cell. In all the experiments, the reactions were followed up to two half lives. The possibilities of direct oxidation of the dye by Mn(II) and its complexation with dye has been tested spectrophotometrically. The findings reveal that Mn(II) undergoes complexation with chloramine-T and not with the dye.

The stoichiometry was determined using varying ratios of oxidant to acridine yellow, thermostatted at 25°C for 48 h. The absorbance at 445 nm was measured and residual CAT was determined idiometrically using standard sodium thiosulfate as titrant and potassium iodide-starch as the indicator. The mole ratio, i.e., no. of moles of oxidant consumed per mol of AY, was calculated.

The representative stoichiometry of reaction can be depicted as:

\[
AY^+ + CAT + H_2O = P^+ + CH_3C_6H_4SO_2NH_2 + CH_3CH_2OH + CH_3CN + 2HCl
\]

where \(P^+ = 7\)-aminoquinoline-2,3-dicarboxylic acid

Product analysis was carried out by mixing 1M sulfuric acid (50 ml), AY+ (300 mg) and CAT (3 g). The mixture was allowed to stand for 24 h. The organic components were partitioned with diethyl ether. Using benzene-ethyl acetate mixture (8:2) as an eluent, preliminary studies were carried out by thin layer chromatography. The IR spectrum of the major separated sample showed absorption peak at 1388 cm\(^{-1}\), which may be due to presence of COO\(^-\) stretching of carboxylic group. This is further supported by the strong absorption band at 1305 cm\(^{-1}\). Presence of carbonyl group is further substantiated by the presence of C-O stretching bands at 1159, 1097 and 1018 cm\(^{-1}\). The absorption band at 1528 cm\(^{-1}\) supports the N-H bending. The absorption peak at 1599 cm\(^{-1}\) supports the C-N stretching. Generally, the O-H stretching band of the carboxylic group gets superimposed upon C-H stretching at 3261 cm\(^{-1}\) of benzene nucleus. The strong absorption peak at 3359 cm\(^{-1}\) indicates the presence of conjugated carboxylic acid. Absence of intense absorption peak at 1300-1200 cm\(^{-1}\) shows the absence of N-O stretching. Therefore, oxidation at nitrogen atom and formation of N-oxide in the heterocyclic ring is unlikely. The main product is thus identified as 7-aminoquinoline-2,3-dicarboxylic acid. We have earlier reported similar products in the case of oxidation of acridine orange dye with acidic chlorite\(^{15}\). Literature survey also reveals that oxidation of acridine by various oxidants such as calcium hypochlorite in the presence of cobalt, bromine and sodium methoxide, potassium permanganate and ozone yields quinoline-2, 3-dicarboxylic acid as a major product\(^{16}\). Studies on further characterization of reaction products are in progress.

**Results and discussion**

In a typical kinetic run, with \([AY^+] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}\), \([\text{CAT}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}\), \([\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}\), a plot of log absorbance versus time is linear indicating that reaction under chosen conditions follows pseudo first order kinetics. The mean pseudo first order rate constant \(k_0\) was found 4.63x10\(^{-4}\) s\(^{-1}\). The concentration of CAT was varied over a wide range, while other reactants were kept constants. Plot of log \(k_0\) versus log CAT gave a straight line with slope 0.73 (0.99), suggesting that the reaction has fractional order dependence with respect to CAT. This kinetic evidence of complex formation between substrate and oxidant further supports the validity of the proposed mechanism. With the employed reactant concentration \([AY^+] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}\), \([\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}\), \([\text{CAT}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}\), the initial ionic strength of reaction mixture was 0.0032. The ionic strength was varied from 0.0032-0.0212 by the addition of sodium sulphate.

The effect of the catalyst on the reaction rate was studied using varied initial concentration of the metal ion. Plot of log [Mn(II)] versus log \(k''\) is linear with a slope 1.03 (\(R^2 = 0.99\)) (Fig. 1) showing that the order in catalyst is one.

The effect of PTS, one of the end products in chloramine-T oxidations on the rate of oxidation was studied by taking various concentrations of PTS, keeping the concentrations of other reactants constant at constant temperature. Oxidation rate decreased with the increase in the concentration of PTS. The decrease in reaction rate supports our consideration that HOCl
is the main oxidizing species in accordance with the following equilibrium\(^\text{(7)}\):

$$\text{ArSO}_2\text{NHCl} + \text{H}_2\text{O} = \text{HOCl} + \text{ArSO}_2\text{NH}_2$$

(PTS)

**Mechanism**

Chloramine-T behaves as a strong electrolyte and in acidic media it furnishes various oxidising species\(^\text{17}\).

$$\text{ArSO}_2\text{NaCl} = \text{ArSO}_2\text{NCl}^- + \text{Na}^+$$ \hspace{1cm} \text{(1)}

$$\text{ArSO}_2\text{NCl}^- + \text{H}^+ = \text{ArSO}_2\text{NHCl}$$ \hspace{1cm} \text{(2)}

(N-Chloro toluene-\(p\)-Sulphonamide)

$$2\text{ArSO}_2\text{NHCl} = \text{ArSO}_2\text{NCl}_2 + \text{ArSO}_2\text{NH}_2$$ \hspace{1cm} \text{(3)}

(Dichloramine-T)

$$\text{ArSO}_2\text{NCl}_2 + \text{H}_2\text{O} = \text{ArSO}_2\text{NHCl} + \text{HOCl}$$ \hspace{1cm} \text{(4)}

(Hypochlorus acid)

In our experimental studies the rate of reaction is retarded by addition of PTS, which suggests that the Eq. (5) must be preceded by the rate determining step. The neutral salt effect supports the participation of neutral molecule in the rate determining step. HOCl acid may be considered as the main oxidizing species for the reaction, which proceeds slowly in sulfuric acid. The linear double reciprocal plot with intercept on Y-axis of \(k^{-1}\) versus CAT\(^{-1}\) suggests the formation of a complex between substrate and oxidant\(^\text{18}\).

**Mechanism for Mn(II) catalyzed reaction**

A few experiments were carried out with initially added Mn(II), and it was observed that the reaction rate increases with the increase in Mn(II) concentration. Catalysis by Mn(II) ions in the case of oxidation by permanganate is well known\(^\text{19}\). The observation that in the absence of oxidizing agent, Mn(II) does not oxidize AY\(^+\) in a direct reaction confirms that reduction of Mn(II) to lower oxidation states does not take place. Higher oxidation states of manganese are involved in the catalytic cycle. The addition of Mn(II) accelerates the rate of reaction and can be explained in the light of following chemical equation:

$$2\text{Mi(II)} + 2\text{ArSO}_2\text{NCl}_2 + 2\text{H}_2\text{O} + 2\text{H}^+ = \text{2ArSO}_2\text{NCl}_2 + 2\text{HOCl} + \text{2ArSO}_2\text{NH}_2 + \text{HCl}$$ \hspace{1cm} \text{(10)}

Mn(III) is a powerful oxidizing agent with a standard reduction potential of 1.15 V (Ref. 20). For
this reaction, Mn(II) is converted to Mn(III) by the oxidation of chloramine-T. The Mn(III) thus formed forms a complex with the dye molecule in step 2, which is more easily oxidized by the oxidizing agent in the catalytic cycle.

\[
AY^+ + \text{Mn(III)} \rightarrow \text{Complex} \quad \ldots(11)
\]

\[
\text{Complex} + 4\text{HOCl} + H_2O \rightarrow P^+ + \text{Mn(II)} + H^+ \quad \ldots(12)
\]

The rate equation for the uncatalyzed reaction between \( AY^+ \) and CAT can be represented as follows

\[
r = -\frac{d[AY^+]}{dt} = k_0 [AY^+] [\text{CAT}]^{2/3} \quad \ldots(13)
\]

When [CAT] is in excess, the above equation reduces to

\[
r = k_0' [AY^+] \quad \ldots(14)
\]

where the pseudo first-order rate constant for uncatalyzed reaction is \( k_0' = k_0 [\text{CAT}]^{2/3} \).

In the presence of the catalyst, the oxidation reaction proceeds through both uncatalyzed and catalyzed pathways. Therefore, Eqs 15 and 16 represent the rate of depletion of \( AY^+ \) in the presence of catalyst under excess [CAT] and acid concentrations.

\[
-\frac{d[AY^+]}{dt} = \{k_0' + k_c' \left[Mn(II)\right]\} [AY^+] \quad \ldots(15)
\]

\[
= k_0'' [AY^+] \quad \ldots(16)
\]

where \( k_c' = k_c [\text{CAT}]^{2/3} \) and \( k_0'' = \{k_0' + k_c' \left[Mn(II)\right]\} \)

References