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# Ru (III) CATALYSED OXIDATIVE DEGRADATION OF TRIARYLMETHANE DYE USING ACIDIC CHLORITE

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## ABSTRACT

The oxidation reaction of $CV^+$ by acidic chlorite exhibits an interesting linear phenomenon. The depletion of $CV^+$ in presence of excess of chlorite ($ClO_2^-$) and ($H^+$) follows an exponential decay involving pseudo-first order kinetics. The catalysed oxidative reaction with Ru (III) also proceeds in the same way. Detailed kinetics has been studied by using spectrophotometric methods. The stoichiometry of the uncatalysed reaction is $CV^+ + 2\ ClO_2^- \rightarrow P_1 + P_2 + 2Cl^-$. Increment in ionic strength by the addition of neutral salt resulted in decrease in rate constant, which indicates the participation of two neutral species in rate determining step. The effect of pH on oxidative mechanism has been reported. Reaction mechanism with reaction dynamics for both uncatalysed and catalysed reaction has been proposed. The catalytic range for Ru (III) was found to be $1.0 \times 10^{-7}$ mol dm$^{-3}$. Role of acid has been found to be complex in nature.

**Key words** : Crystal violet, Chlorite, Ru (III), Catalysis, Oxidation

## INTRODUCTION

The chemistry of chlorite ion has been the subject of extensive studies due to its disproportionation into different products under various pH conditions and also its applications as disinfectant in water treatment[1-3]. Literature survey reveals disproportionation of chlorite in the presence of various cations but very little is known about the catalyzed oxidation involving $ClO_2^-$ ion and $CV^+$. Crystal violet is a nontoxic water-soluble dye of triphenylmethane class having sharp absorption peak at $\lambda_{max}$ 595 nm in visible region that makes it an ideal substrate for spectrophotometric monitoring. In weakly acidic solution, it shows violet color and in strongly acidic solution, green color ; while in highly strong acidic medium, yellow color is visualized. The reaction of $CV^+$ with

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acidic $ClO_2^-$ catalyzed by Ru (III) have been exploited to utilize it as an indicator reaction in the determination of trace amount of Ru (III). The present study gives the dynamics of $CV^+$ linear consumption in presence of $ClO_2^-$ and Ru (III).

## EXPERIMENTAL

The chemicals used were of analytical grade (Aldrich, B. D. H.) and double distilled water was used throughout to prepare the solutions. An aqueous solution of chlorite (Aldrich) was prepared afresh each time. The aqueous solution M/1000 of $CV^+$ was prepared by dissolving 0. 4079 g of $CV^+$ in 100 mL of double distilled water. Stock solution of $H_2SO_4$ was prepared by diluting the calculated volume (from specific gravity) of acid with double distilled water and finally its concentration was determined by titrating it against standard NaOH solution. Ru(III) stock solution (0. 02M) was prepared as reported earlier[4].

### Kinetic procedure

In all the experiments, the pseudo-first-order kinetics with respect to crystal violet were monitored at 595 nm, using Systronicrcs Vis spectrophotometer. Beer's law was valid for the measurement under the experimental conditions considered. No interference from the reagents, intermediates or products was observed at 595 nm. The total initial volume of the reaction mixture was always kept 10 mL and at $25.0 \pm 0.1^0$C. Reagent solutions were mixed in the sequential order : Requisite volumes of crystal violet, sulphuric acid, plus water or other reagents, wherever necessary. Separately thermostatic solution of $NaClO_2$ was added to commence the reaction. After vigorous mixing, solution was transferred to spectrophotometer cell. In all the experiments, the reactions were followed up to two half lives. A constant ionic strength of the reaction mixture was maintained by adding required amount of sodium sulphate solution.

### Stoichiometry and product analysis

Crystal violet (300 mg / 250 mL water), sulphuric acid (15 mL of 1 M/ 100 mL) and $NaClO_2$ (500 mg/ 150 mL) were mixed for the product analysis. After the reaction time of 24 hr, the organic components were separated from the mixture into ether. The ether extract was dried and concentrated using rotary evaporator, under low pressure. Using benzene : ethyl acetate mixture (8 : 2) as an eluent, preliminary studies were carried out by thin layer chromatography. Stoichiometry was determined using 1 : 10 and 1 : 20 molar ratio of $[CV^+]$ to chlorite with excess of $[H^+]$. After 6 hr, the absorbance at 595 nm was measured and residual $NaClO_2$ was determined iodometrically using standard sodium thiosulfate as titrant and potassium iodide-starch as an indicator. Crystal violet and chlorite ion react in stiochiometry as follows :

$$CV^{+} + 2\,ClO_2^{-} \longrightarrow P_1 + P_2 + H^{+} + 2Cl^{-} \qquad ...(1)$$

Where $P_1$ = 4-Anilinobenzoic acid

$P_2$ = 4, 4' -Diphenoquinone- 4, 4 (bis)-arylimine.

These products have been reported in the case of oxidation of thymol blue by bromate[1], malachite green by persulphate[5] and oxidation of aniline blue by bromate[6].

## RESULTS AND DISCUSSION

The addition of acid causes change in the structure of $CV^{+}$, and therefore, the absorbance decreases on addition of $1.0 \times 10^{-2}$ mol $dm^{-3}$ of acid to the dye solution while λmax remains constant.

With reactant concentration, $[CV^{+}] = 1.0 \times 10^{-5}$ mol $dm^{-3}$, $[H^{+}] = 1.0 \times 10^{-2}$ mol $dm^{-3}$ and $[ClO_2^{-}] = 2.0 \times 10^{-4}$ mol $dm^{-3}$, a plot of log absorbance versus time is linear indicating that reaction has pseudo-first order kinetics and order w. r. t. $CV^{+}$ is unity. The mean pseudo-first order constant was found $2.5 \times 10^{-4}\ s^{-1}$.

### Effect of $H^{+}$ and chlorite ions

An increment in rate of reaction was observed with increase in initial concentration of chlorite and $H^{+}$ ions. The results obtained at constant ionic strength with varied concentrations of sodium chlorite (Fig. 1) and $H^{+}$ ions are reported. The rate of reaction increases with increase in chlorite and $H^{+}$ ions concentration. The plots of log k versus log [oxidant] gave straight lines with slopes 1. 0091 ($R^2 = 0.959$), suggesting the reaction has first-order dependence. The plot of log absorbance versus log [oxidant] at constant substrate and acid concentration is linear with definite intercept with a positive slope suggests the complex formation and showing the validity of the proposed mechanism. The fractional order with respect to $H^{+}$ ion indicates the minor effect of acid on catalytic oxidation.

### Effect of variation in ionic strength

With reactant concentrations, $[CV^{+}] = 1.0 \times 10^{-5}$ mol $dm^{-3}$, $[H^{+}] = 1.0 \times 10^{-2}$ mol $dm^{-3}$ and $[ClO_2^{-}] = 2.0 \times 10^{-4}$ mol $dm^{-3}$, the initial ionic strength of the reaction mixture was 0. 0301. An increase in ionic strength from 0. 0301 to 0. 2701 caused a reduction in rate constant values from 2. 5 x $10^{-4}$ $s^{-1}$ to 0. 99 x$10^{-4}$ $s^{-1}$. The plot of $\sqrt{\mu}$ versus log k was found to be linear with slope - 0. 0005 ($R^2$ = 0. 98); thus, confirming the participation of two oppositely charged species in rate determination step.

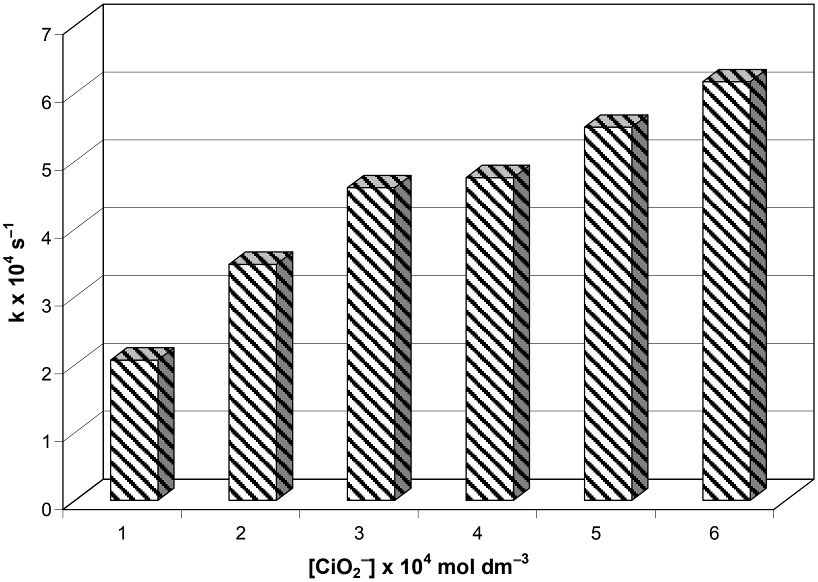


**Fig. 1. Rate constants for different concentration of [$ClO_2^-$] : [$CV^+$] = 1. 0 x $10^{-5}$ mol $dm^{-3}$, [$H^+$] = 1. 0 x $10^{-2}$ mol $dm^{-3}$**

## Effect of Ru (III)

The catalytic efficiency of Ru (III) on the reaction was studied using varied initial conc. of the metal ion. Fig. 2 represents the increment in rate of oxidation of dye with increase in concentration of metal ion. Plot of log [Ru (III)] vs log k gave a straight line with slope 0. 96 ($R^2$ = 0. 99) indicating first order reaction with respect to catalyst.

## Uncatalyzed reaction mechanism

The observed orders with respect to $H^+$, $ClO_2^-$ and $CV^+$ and the negative salt effect suggest that the rate determining step is the reaction between the two oppositely charged species followed by protonation. The oxidation of crystal violet results in the disruption of the conjugate structure; possibly the formation of a carbocation followed by the formation of $P_1$ (4-Anilino benzoic acid) and an intermediate **I** (4, 4' - Dianilino bimethyl) (Fig. 2).

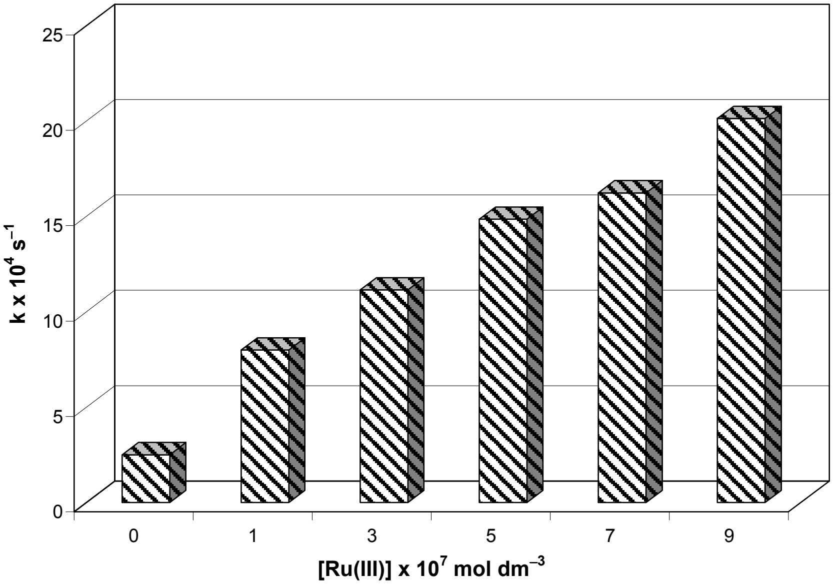


**Fig. 2. Rate constants for different concentration of Ru (III) : $[CV^+] = 1.0 \times 10^{-5}$ mol $dm^{-3}$, $[H^+] = 1.0 \times 10^{-2}$ mol $dm^{-3}$ and $[ClO_2^-] = 2.0 \times 10^{-4}$ mol $dm^{-3}$**

The next possibility is that an attack by HOCl results in further oxidation of the intermediate **I,** to the product $P_2$. As reported earlier in the literature, oxidation by chlorite involves various chloro and oxy-chloro species. $ClO_2$ formation is fast and autocatalytic in HOCl. The stoichiometry of chlorine dioxide formation is dependent on initial chlorite concentration[2,7]. The autocatalysis of HOCl is explained by the asymmetric reactive intermediate $Cl_2O_2$, which yields two HOCl through a second order decomposition or through reaction with chlorite ions. Chlorite ions may add to the formation of HOCl, at high acid concentration, but because of its slow rate and chloride concentration, its constitution will be small[2,8]. Based on the known chemistry of acidic chlorite reactions, the following reactions used to be considered[7–9].

$$ClO_2^- + H^+ \rightleftharpoons HClO_2 \qquad ...(2)$$

$$HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O \qquad ...(3)$$

$$Cl_2 + 2\,ClO_2^- \longrightarrow 2\,ClO_2 + 2\,Cl^- \qquad ...(4)$$

$$Cl_2O_2 + 2\,ClO_2^- + 2\,H^+ \rightleftharpoons 2\,ClO_2 + 2\,HOCl \qquad ...(5)$$

$$HOCl + ClO_2 + H^+ \rightleftharpoons Cl_2O_2 + H_2O \quad ...(6)$$

$$HClO_2 + H^+ + Cl^- \longrightarrow 2\,HOCl \quad ...(7)$$

$$CV^+ + Cl_2 + H_2O \longrightarrow P_1 + I + H^+ + 2\,HCl \quad ...(8)$$

$$I + Cl_2 \longrightarrow P_2 + 2\,H^+ + 2\,Cl^- \quad ...(9)$$

$$CV^+ + H_2O + Cl_2O_2 \longrightarrow P_1 + I + HOCl + H^+ \quad ...(10)$$

$$I + HOCl \longrightarrow P_2 + H^+ + Cl^- + H_2O \quad ...(11)$$

## Ru (III) catalysed mechanism

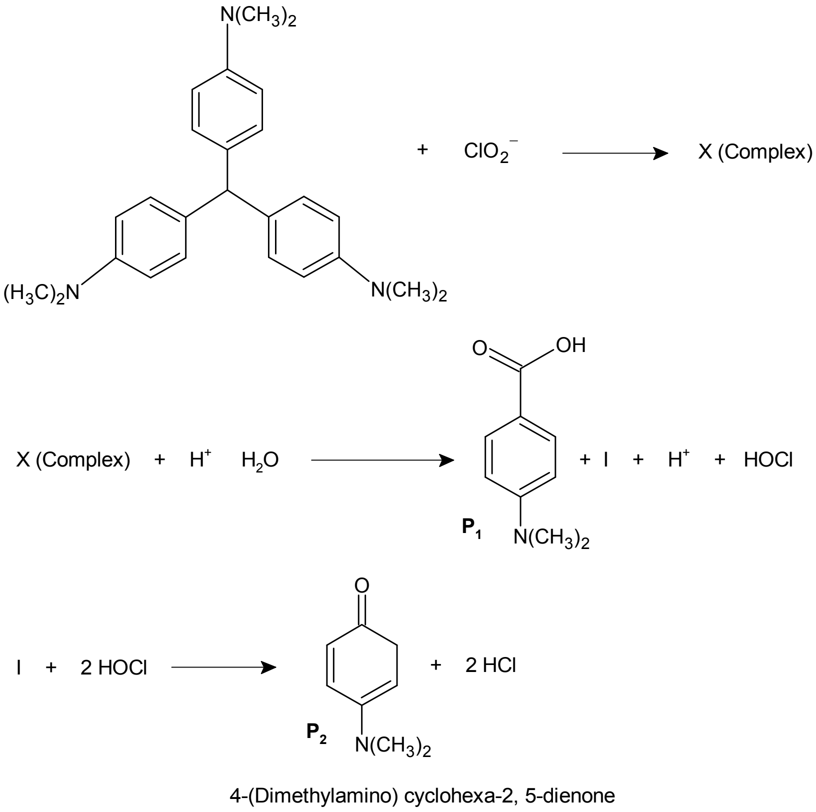
The observation that in absence of oxidizing agent, Ru (III) does not oxidize $CV^+$ in a direct reaction, confirms that reduction of Ru (III) to lower oxidation states does not happen. Higher oxidation states of ruthenium are involved in the catalytic cycle. In absence of dye, the presence of catalytic concentrations of Ru(III) can initiate rapid disproportionation of chlorite in acidic solution, which also confirms that Ru (III) is oxidised to a higher oxidation state in the catalytic cycle. The formation of Ru (V) during the $RuCl_3$ catalysed reactions of alkenes by peracetic acid has been reported by Lee et al.[10] and Kumiya et al.[11]. It is suggested that Ru (III) forms complex with acidic chlorite in a rapid reaction and gets oxidized to Ru (V). The rate limiting step for the catalysed reaction is the reaction between the binary complex and the organic substrate to form ternary complex, in which Ru (V) abstracts electrons from substrate and transfers to the chlorite in the complex[12–14]. It is possible that Ru ions act as electron mediators only within the ternary complex[16–18].

$$\text{Ru (III)} + ClO_2^- \longrightarrow \text{[Binary complex]} \quad ...(12)$$

$$\text{[Binary complex]} + Ac^+ \longrightarrow \text{[Ternary complex]} \quad ...(13)$$

$$\text{[Ternary complex]} + H^+ \longrightarrow \text{Ru (III)} + Ac^+ \quad ...(14)$$

The remaining reaction follows same chemistry as that of uncatalyzed reaction. Chemistry of reaction scheme is same as for the uncatalyzed reaction. Uncatalyzed reaction between $CV^+$ and acidic chlorite is given by Eq. (15).



**Scheme 1**

$$- d[CV^+]/dt \ = \ k_0[CV^+][\ ClO_2^-]^{1/2} \qquad \ldots(15)$$

when $[ClO_2^-]$ I in excess, Eq. (15) reduces to $r = k^{'}_0[CV^+]$ …(16)

where the pseudo-first order rate constant for the uncatalyzed reaction is $k^{'}_0 = k_0[ClO_2^-]^{1/2}$.

Both catalyzed and uncatalyzed pathways are responsible for the oxidation of dye in the presence of catalyst. In presence of excessive chlorite and acid concentration, Eq. (17) and (18) can represent these reactions.

$$- d[CV^+]/dt \ = \ \{k'_0{}' + k_c'CV^+][Ru(III)] \qquad \ldots(17)$$

$$\text{Where } k_c' = k_c\ [ClO_2^-]^{1/2} = \ k''\ [CV^+]$$

$$\text{where } k'' = \{k'_o + k_c'[Ru(III)]\} \qquad \ldots(18)$$

## CONCLUSION

The kinetic study of catalyzed and catalyzed reactions provide plausible mechanism for the oxidation of crystal violet dye. Water soluble dye has a decrease in intensity due to change in pH with no change in λmax. Its reactions in acidic chloride and Ru (III) provide insight into scope of treatment of toxic water soluble pollutants and role of auxiliary compounds, when present in wastewater from industries.

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