

# Kinetics and Mechanistic Studies of Oxidation of Tartaric Acid by diperiodatocuprate(III) in Aqueous Alkaline Medium

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**Abstract:** - The kinetics of oxidation of tartaric acid (TA) by diperiodatocuprate(III) (DPC) in aqueous alkaline medium at a constant ionic strength of  $0.05 \text{ mol dm}^{-3}$  was studied spectrophotometrically. The main oxidation product was identified as methanal (HCHO). The stoichiometry was found to be 1:2 ([TA] : [DPC]). The order of reaction with respect to [DPC] and [TA] was unity. The rate decreased with increase in [OH<sup>-</sup>] and [IO<sub>4</sub><sup>-</sup>] over the concentration range studied. The ionic strength and dielectric constant of the medium did not affect the rate significantly. Based on the experimental results, a possible mechanism involving free radicals was proposed. The activation parameters were determined and discussed. Kinetics study suggests that the active species of DPC is found to be monoperiodatocuprate(III), [Cu(OH)<sub>2</sub>(H<sub>3</sub>IO<sub>6</sub>)].

**Keywords:** Oxidation, Diperiodatocuprate(III), Tartaric acid, Spectroscopy; Kinetics

## I. INTRODUCTION

Tartaric acid (TA) and its derivatives have a plethora of uses in the field of pharmaceuticals. For example, it has been used in the production of effervescent salts, in combination with citric acid, to improve the taste of oral medications [1]. The potassium antimonyl derivative of the acid known as tartar emetic is included, in small doses, in cough syrup as an expectorant. Tartaric acid also has several applications for industrial use. The acid has been observed to chelate metal ions such as calcium and magnesium. Therefore, the acid has served in the farming and metal industries as a chelating agent for complexing micronutrients in soil fertilizer and for cleaning metal surfaces consisting of aluminium, copper, iron, and alloys of these metals, respectively [2].

Transition metals in their higher oxidation states can generally be stabilized by chelation with suitable polydentate ligands. These metal chelates such as diperiodatocuprate(III) [3] (DPC), diperiodatoargentate(III) [4] (DPA) and diperiodatonickelate(IV) [5] (DPN) are good oxidants in a medium with an appropriate pH value. Diperiodatocuprate(III) is a versatile one-electron oxidant and the oxidation study of DPC is scanty in view of its limited solubility and stability in aqueous medium. Its use as an analytical reagent is now well recognized [6]. Copper complexes have a major role in oxidation chemistry due to their abundance and relevance in

biological chemistry [7, 8]. Copper(III) is involved in many biological electron transfer reactions [9]. When copper(III) periodate complex (DPC) is the oxidant and multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is the active oxidant.

Literature survey reveals that there are no reports on the mechanistic studies of tartaric acid oxidation by DPC. Such oxidation studies may throw some light on the mechanism of conversions of the compounds in biological systems. In earlier report of DPC oxidation [3], the order in [OH<sup>-</sup>] was found to be less than unity and periodate had a retarding effect in most of reaction. However in the present study we have observed different kinetics observations. The present investigation is aimed to know the kinetics of redox chemistry of Cu(III), reactivity of TA towards DPC in such media and also to arrive at a plausible mechanism on the basis of kinetic results. An understanding of the mechanism allows the chemistry to be interpreted, understood and predicted.

## II. EXPERIMENTAL

### 2.1. Materials and reagents

All chemicals used were of analytical grade. Double-distilled water was used throughout the work. The solution of tartaric acid (Bayer, AG) was prepared by dissolving known amount of compound and further diluted to  $100 \text{ cm}^3$  with double-distilled water. KNO<sub>3</sub> and KOH (BDH, AR) were used to maintain the ionic strength and alkalinity of the reaction, respectively. The copper(III) periodate complex was prepared by standard procedure [10]. Existence of copper(III) complex was verified by its UV-Vis spectrum, which showed three absorption bands with maximum absorption at 418nm shown in (fig.1) The aqueous solution of copper(III) was standardized by iodometric titration and gravimetrically by the thiocyanate [11] method. The copper(II) solution was prepared by dissolving the known amount of copper sulfate (BDH) in distilled water. Periodate solution was prepared by weighing the required amount of sample in hot water and used after keeping it for 24h. Its concentration was ascertained iodometrically [12] at neutral pH by phosphate buffer solution.

## 2.2. Instruments

The kinetic measurements were carried out on Varian CARY 50 Bio UV–Vis spectrophotometer (Varian, Victoria-3170, Australia). For pH measurement an Elico pH meter model LI 120 was used.

## 2.3. Kinetic measurements

The kinetics of oxidation of tartaric acid was followed under pseudo-first order condition where,  $[TA] > [DPC]_i$  at  $25 \pm 0.1^\circ\text{C}$ . The reaction was initiated by mixing thermally equilibrated DPC with tartaric acid solution, with required concentrations of KOH,  $\text{KNO}_3$  and  $\text{KIO}_4$  and progress of the reaction was followed spectrophotometrically at 418nm by monitoring the decrease in the absorbance due to DPC with molar absorption index,  $\epsilon = 6240 \pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . It was also verified that interference from other species in the reaction mixture at the wavelength 418nm was negligible.

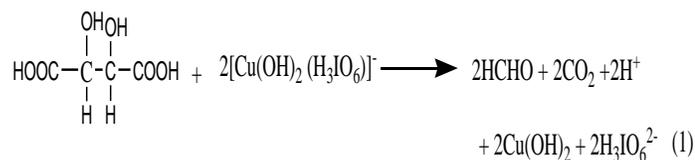
The rate constants,  $k_{\text{obs}}$  were obtained from the plot of log (absorbance) versus time plots and the rate constants were reproducible within  $\pm 5\%$  error. All the kinetic runs were followed more than 70% completion of reaction. During the kinetics, a constant concentration, viz.,  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$  of  $\text{KIO}_4$  was used throughout the experiment.  $k_{\text{obs}}$  values were the average of duplicate measurements and when necessary, triplicate measurements were performed.

In view of the modest concentration of alkali used in the reaction medium, attention was also directed to the effect of the reaction vessel surface on the kinetics. Use of polythene/acrylic wares and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the reaction rates. The spectroscopic changes during the reaction are shown in Fig 2. It is evident from the Fig. 2 that the concentration of DPC decreases at 418 nm. Regression analysis of the experimental data to obtain the regression coefficient  $r$  and standard deviation  $S$  of points from the regression line was performed using Microsoft 2003 Excel program.

## III. RESULTS

### 3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPC to TA in the presence of constant amount of  $\text{OH}^-$  and  $\text{KNO}_3$  in the reaction were kept for 2h in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was estimated spectrophotometrically at 418 nm. The results indicated 1:2 stoichiometry (TA: DPC) as given in Eq. 1.



The product analysis was carried out under kinetic conditions. The presence of aldehyde and/or ketone was characterised by the reaction with 2,4-dinitro-phenylhydrazine and the Tollens reagent displayed to be positive for aldehyde [13]. Brisk effervescence was observed when product is treated with dil HCl which confirms that byproduct  $\text{CO}_2$  was evolved. To find yield of aldehyde under these experimental conditions, when  $[TA]$  is more than  $[DPC]$ , after an hour, the reaction mixture was cooled in ice bath to which the excess of 2,4-DNP solution was added and the mixture was stored overnight in the refrigerator. The precipitated 2,4-DNP product was filtered through weighed crucible, dried and weighed. A blank using aldehyde under the same experimental conditions was also run; it was found that the yield was 52% of the theoretical. The melting point of 2,4-DNP derivative was observed as  $154^\circ\text{C}$  which confirms that product is formaldehyde-2,4-dinitro-phenylhydrazone (lit. m.p. 153-156  $^\circ\text{C}$ ). The same product was obtained for the oxidation of tartaric acid in earlier work [14]. Another product, Cu(II) was identified by UV-Vis spectral data. The reaction products did not undergo further oxidation under the present kinetic conditions.

### 3.2. Reaction orders

The reaction orders were determined from the slope of log  $k_{\text{obs}}$  versus log (concentration) plots by varying the concentration of TA, alkali, and periodate in turn, while keeping all other concentrations and conditions constant.

### 3.3. Influence of concentration of DPC on the reaction rate

The concentration of the oxidant, DPC was varied in the range of  $2.0 \times 10^{-5}$  to  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$  at constant concentrations of TA,  $\text{OH}^-$  and  $\text{IO}_4^-$ . The fairly constant  $k_{\text{obs}}$  values (Table 1) indicate that the order with respect to DPC concentration was unity. This was also confirmed by the linearity of the plots of log(Abs) versus time upto 70% completion of reaction. Individual plots of log(abs) versus time for different initial concentration of DPC display parallel and linearity (Fig. 3).

### 3.4. Influence of concentration of tartaric acid on the reaction rate

The effect of tartaric acid was studied in the range of  $2.0 \times 10^{-4}$  to  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$  and at constant concentrations of DPC, alkali and ionic strength. The rate of the reaction increased with increase in concentration of TA (Table 1). The order with respect to TA concentration was obtained from the plot of log  $k_{\text{obs}}$  versus log  $[TA]$  and found to be unity (1.08) (Fig. 4).  $k_2$  ( $k_{\text{obs}} / [TA]$ ) values calculated were nearly constant.

### 3.5. Influence of concentration of alkali on the reaction rate

The effect of alkali concentration with rate of reaction was studied in the range of  $0.4 \times 10^{-2}$  to  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$  and at constant concentrations of DPC, TA and ionic strength. The rate of the reaction decreased with increase in the

concentration of alkali (Table 1). The order with respect to alkali concentration was obtained from the plot of  $\log k_{\text{obs}}$  versus  $\log [\text{OH}^-]$  and was found to be  $-0.44$ .

### 3.6. Influence of concentration of $\text{IO}_4^-$ on the reaction rate

The effect of periodate concentration was studied in the range of  $0.1 \times 10^{-4}$  to  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$  at  $25^\circ\text{C}$  and at constant concentrations of DPC, TA, alkali and ionic strength. The rate of the reaction decreased with increase in the concentration of  $\text{IO}_4^-$  (Table 1), which shows that periodate retards the rate of reaction. The order with respect to  $[\text{IO}_4^-]$  was found to be  $-0.41$ .

Under the experimental conditions, the rate law is given as,

$$\text{Rate} = k_{\text{obs}} [\text{DPC}] [\text{TA}]^{1.04} [\text{OH}^-]^{-0.44} [\text{IO}_4^-]^{-0.41}$$

(Here  $k_{\text{obs}}$  refers to the observed rate constant under the experimental conditions).

### 3.7. Effect of initially added products

The externally added products, copper(II) ( $\text{CuSO}_4$ ) and formaldehyde in the range  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  did not have any significant effect on the rate of the reaction.

### 3.8. Polymerization study

The intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile monomer was initially added, was kept for 2 h in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either DPC or TA alone with acrylonitrile did not induce any polymerization under the same condition as those induced for the reaction mixture. Initially added acrylonitrile decreased the rate of reaction indicating free radical intervention, which is the case in earlier work [15].

### 3.9. Effect of ionic strength (I) and dielectric constant (D) on the reaction rate

The addition of  $\text{KNO}_3$  at constant  $[\text{DPC}]$ ,  $[\text{TA}]$ ,  $[\text{OH}^-]$ , and  $[\text{IO}_4^-]$  was found that increasing ionic strength had negligible effect on the rate of the reaction. Dielectric constant of the medium, D, was varied by varying percentage of water and t-butyl alcohol. The D values were calculated from the equation  $D = D_w V_w + D_B V_B$ , where  $D_w$  and  $D_B$  are dielectric constants of pure water and t-butyl alcohol, respectively, and  $V_w$  and  $V_B$  are the volume fractions of components water and t-butyl alcohol, respectively, in the mixture. The decrease in dielectric constant of the reaction medium had no effect on the rate of reaction. The oxidation of water and t-butyl alcohol mixture with DPC under the experimental conditions did not occur.

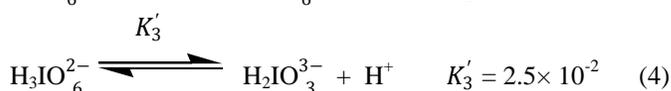
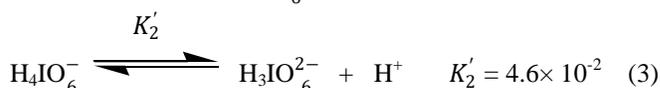
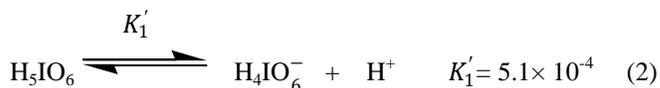
### 3.10. Effect of temperature

The rate of the reaction was measured at four different temperatures under varying concentrations of TA,

alkali and periodate, keeping other conditions constant. The data were subjected into least square analysis given in tables 2A and 2B. From the plot of  $\log k_{\text{obs}}$  vs  $1/T$ , activation energy,  $E_a$  was obtained and other activation parameters have also been calculated and tabulated in tables 2A and 2B. The comparison of activation parameters for the oxidation of TA by Vanadium(V) [14], is shown in table 2B. The low value of enthalpy of activation in DPC oxidation shows more favourable reaction in DPC.

## IV. DISCUSSION

The water soluble copper(III) periodate complex is reported [16] to be  $[\text{Cu}(\text{HIO}_6)_2(\text{OH})_2]^{7-}$ . However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as  $\text{HIO}_6^{4-}$  (as present in the complex) as is evident from its involvement in the multiple equilibria [16] ((2)–(4)) depending on the pH of the solution.

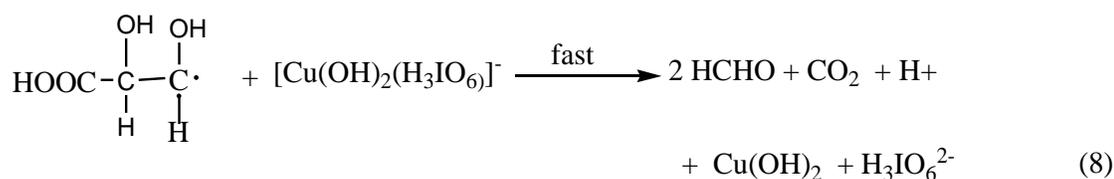
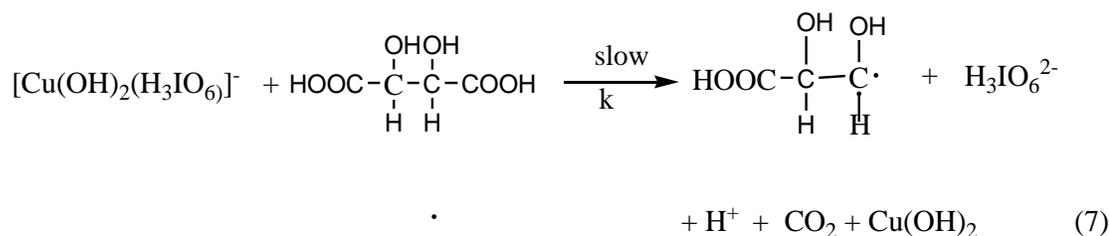
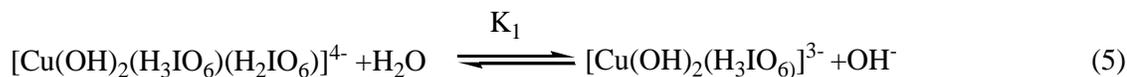


Periodic acid exists in acid medium as  $\text{H}_5\text{IO}_6$  and as  $\text{H}_4\text{IO}_6^-$  around pH 7. Thus, under the conditions employed in alkaline medium, the main species are expected to be  $\text{H}_3\text{IO}_6^{2-}$  and  $\text{H}_2\text{IO}_6^{3-}$ . At higher concentrations, periodate also tends to dimerize [6]. However, formation of this species is negligible under conditions employed for kinetic study. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate (III),  $[\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)_2]^{3-}$ , also supported by earlier work [16-17].

The reaction between the diperiodatocuprate(III) complex and TA in alkaline medium has the stoichiometry 1:2 (TA:DPC) with a first-order dependence on  $[\text{DPC}]$  and  $[\text{TA}]$ , negative fractional order dependence on the [alkali] and periodate. No effect of added products was observed. Based on the experimental results, a mechanism is proposed for which all the observed orders in each constituent such as [oxidant], [reductant],  $[\text{OH}^-]$ , and  $[\text{IO}_4^-]$  may be well accommodated. Lister [18] proposed three forms of copper(III) periodate in alkaline medium as diperiodatocuprate(III) (DPC), monoperiodatocuprate(III) (MPC), and tetrahydroxocuprate(III). Hence, in the present study, DPC and MPC are to be considered as active forms of copper(III) periodate complex.

In most of the reports [17, 18] on DPC oxidation, periodate had a retarding effect and  $\text{OH}^-$  had an increasing effect on the rate of the reaction. However in the present kinetic study, different kinetic results have been obtained. In

this study both  $\text{OH}^-$  and periodate retarded the rate of the reaction. The result of decrease in rate of reaction with increase in alkalinity (Table 1) can be explained in terms of prevailing equilibrium of formation of  $[\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)]^{3-}$  from  $[\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{4-}$  hydrolysis as given in Eq. (5) of Scheme 1.



**Scheme 1** Mechanism for the oxidation of TA by alkaline DPC

Such types of equilibria (5) and (6) of scheme 1, have been well noted in the literature [19]. It may be expected that a lower periodate complex such as monoperiodatocuprate(III) (MPC) is more important in the reaction than the DPC in view of its participation in the reaction as given in scheme 1. The inverse fractional order in  $\text{H}_3\text{IO}_6^{2-}$  might also be due to this reason. Therefore, MPC might be the main reactive form of the oxidant.

Since Scheme 1 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in the literature [20].

Also, the decrease in rate with increase in  $\text{H}_3\text{IO}_6^{2-}$  (Table 1) suggests the displacement of periodate species to form monoperiodatocuprate(III) (MPC) species as given in Eq. (6) of Scheme 1.

The oxidation reaction proceeds via formation of a free radical derived from tartaric acid in the slow step. This free radical in the subsequent fast steps reacts with one more mole of MPC to form formaldehyde, which eliminates totally two molecules of carbon dioxide. Scheme 1 leads to the rate law (10), (see appendix)

$$\text{rate} = -\frac{d[\text{DPC}]}{dt} = \frac{kK_1K_2[\text{TA}][\text{DPC}]_T}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-] + K_1[\text{H}_3\text{IO}_6^{2-}] + K_1K_2} \rightarrow (10)$$

This explains all the observed kinetic orders of different species. TA shows unit order since the concentration term of TA was present in numerator only. The negative less than unit order in alkali and periodate concentrations are explained by the presence of  $[\text{OH}^-]$  and  $[\text{IO}_4^-]$  terms in the denominator

only, shown in equation.(10). The equation (10) is also written as equation(11).

$$k_{obs} = \frac{rate}{[DPC]} = \frac{kK_1K_2[TA]}{[H_3IO_6^{2-}][OH^-] + K_1[H_3IO_6^{2-}] + K_1K_2} \rightarrow (11)$$

The equation(11) for  $k_{obs}$  can be rearranged into equation(12), which is suitable for verification.

$$\frac{1}{k_{obs}} = \frac{[H_3IO_6^{2-}][OH^-]}{kK_1K_2[TA]} + \frac{[H_3IO_6^{2-}]}{kK_2} + \frac{1}{k[TA]} \rightarrow (12)$$

According to equation (12), the plots of  $1/k_{obs}$  vs  $1/[TA]$ , ( $r \geq 0.999$ ,  $S \leq 0.011$ ),  $1/k_{obs}$  vs  $1/[OH^-]$  ( $r \geq 0.995$ ,  $S \leq 0.013$ ) and  $1/k_{obs}$  vs  $[H_3IO_6^{2-}]$  ( $r \geq 0.926$ ,  $S \leq 0.019$ ) should be linear and are found to be so (Fig.5).

The values of enthalpy of activation  $\Delta H^\ddagger$ , entropy of activation  $\Delta S^\ddagger$  and free energy of activation  $\Delta G^\ddagger$  were calculated. These values are given in Table 2A and 2B. The value of  $\Delta S^\ddagger$  is within the range for a radical reaction and has been ascribed to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of rigid transition state [21]. The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as higher rate constant of the slow step, indicate that the oxidation presumably occurs via inner-sphere mechanism [22]. The effect of ionic strength and dielectric constant on the rate explains qualitatively the involvement of a neutral molecule in the reaction, as depicted Scheme 1.

## V. CONCLUSIONS

The kinetics of the diperiodatocuprate(III) oxidation of tartaric acid in alkaline medium was investigated using the spectrophotometric technique at different temperatures. Among the various species of DPC in an alkaline medium,  $[Cu(OH)_2(H_3IO_6)]^-$  was considered to be the active species for the title reaction. The results indicated that the role of pH in the reaction medium is crucial. Temperature effect and activation parameters were evaluated. The overall mechanistic sequence described here is consistent with all the experimental evidences including the product, spectral, mechanistic and kinetic studies.

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### Appendix

According to Scheme 1

$$\begin{aligned} \text{Rate} &= -\frac{d[\text{DPC}]}{dt} \\ &= \frac{k K_1 K_2 [\text{TA}] [\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{4-}}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-]} \rightarrow (\text{A. 1}) \end{aligned}$$

Total concentration of DPC is given by

$$\begin{aligned} [\text{DPC}]_{\text{T}} &= [\text{DPC}]_{\text{f}} + [\text{DPC}]^{3-} + [\text{DPC}]^{-} \\ &= [\text{DPC}]_{\text{f}} + K_1 \frac{[\text{DPC}]}{[\text{OH}^-]} + \frac{K_1 K_2 [\text{DPC}]}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-]} \\ &= [\text{DPC}]_{\text{f}} \left[ 1 + \frac{K_1}{[\text{OH}^-]} + \frac{K_1 K_2}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-]} \right] \\ [\text{DPC}]_{\text{T}} &= [\text{DPC}]_{\text{f}} \left[ \frac{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-] + K_1[\text{H}_3\text{IO}_6^{2-}] + K_1 K_2}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-]} \right] \\ [\text{DPC}]_{\text{f}} &= \frac{[\text{DPC}]_{\text{T}} [\text{H}_3\text{IO}_6^{2-}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-] + K_1[\text{H}_3\text{IO}_6^{2-}] + K_1 K_2} \rightarrow (\text{A. 2}) \end{aligned}$$

$$[\text{OH}^-]_{\text{T}} = [\text{OH}^-]_{\text{f}} + [\text{DPC}]^{3-} + [\text{DPC}]^{-}$$

$$[\text{OH}^-]_{\text{T}} = [\text{OH}^-]_{\text{f}} + \frac{K_1 [\text{DPC}]}{[\text{OH}^-]} + \frac{K_1 K_2 [\text{DPC}]}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-]}$$

In view of low concentration of DPC, 2<sup>nd</sup> and 3<sup>rd</sup> terms are neglected.

$$\therefore [\text{OH}^-]_{\text{T}} = [\text{OH}^-]_{\text{f}} \rightarrow (\text{A. 3})$$

Substituting (A.2) and (A.3) in (A.1), we get,

$$\text{Rate} = \frac{k K_1 K_2 [\text{TA}] [\text{DPC}]_{\text{T}}}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-] + K_1[\text{H}_3\text{IO}_6^{2-}] + K_1 K_2} \rightarrow (\text{A. 4})$$

### FIGURE LEGENDS

**Fig. 1** UV-Vis spectrum of diperiodatocuprate(III) in aqueous solution at 25 °C ([DPC] = 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>)

**Fig.2** UV-Vis spectra changes during the oxidation of tartaric acid (TA) by alkaline diperiodatocuprate(III) (DPC) at 298K, [DPC]=1.0×10<sup>-4</sup>, [TA]=1.0×10<sup>-3</sup>, [OH<sup>-</sup>]=0.02, [IO<sub>4</sub><sup>-</sup>]=5.0× 10<sup>-5</sup> and I=0.05 mol dm<sup>-3</sup> with scanning time interval of 1min.

**Fig. 3** First order plots for the oxidation of tartaric acid by DPC in an aqueous alkaline medium at 27<sup>o</sup>C, 10<sup>5</sup> [DPC] (mol dm<sup>-3</sup>); (1)2.0; (2)5.0; (3)10.0; (4)15.0; (5)20.0.

**Fig. 4** Plot of log k<sub>obs</sub> versus log [TA]

**Fig. 5** Verification of rate law (11) in the form of equation (12) for the oxidation of tartaric acid by diperiodatocuprate(III) in an aqueous alkaline medium at 27 °C (A) Plot of 1/k<sub>obs</sub> vs, 1/[TA] , (B) Plot of 1/k<sub>obs</sub> vs, [OH<sup>-</sup>] and (C) Plot of 1/ k<sub>obs</sub> vs, [IO<sub>4</sub><sup>-</sup>]

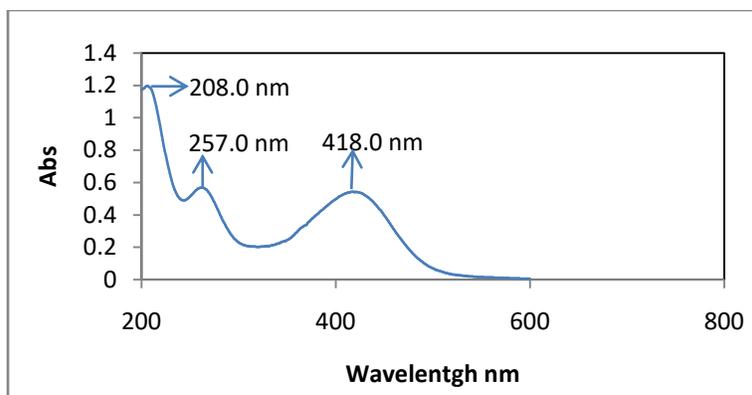


Fig.1

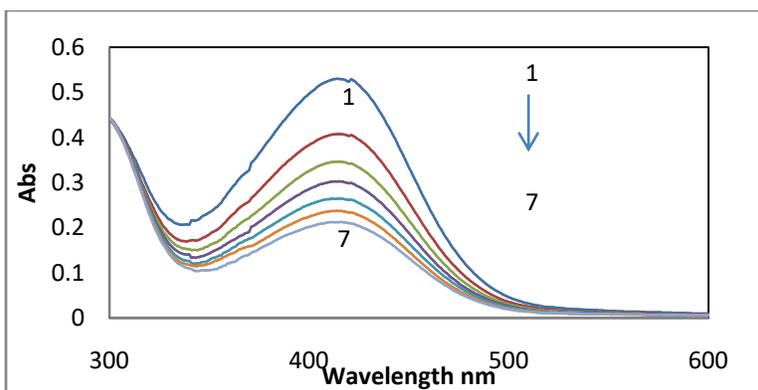


Fig.2

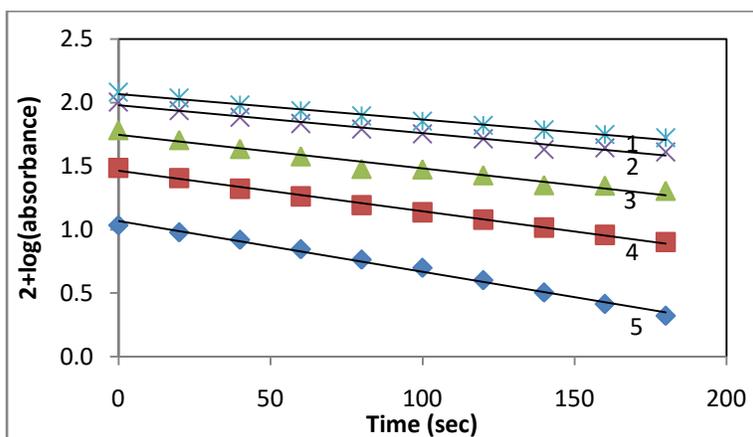


Fig.3

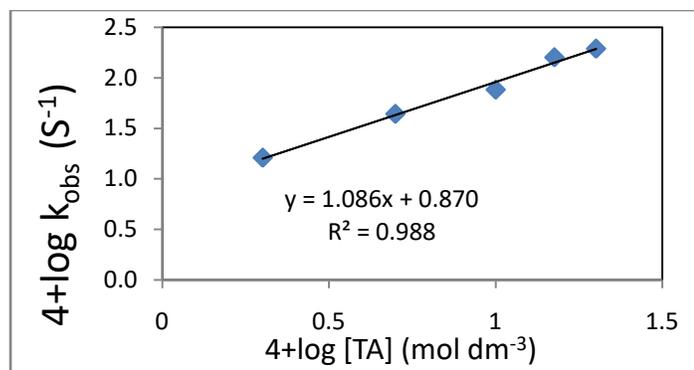


Fig.4

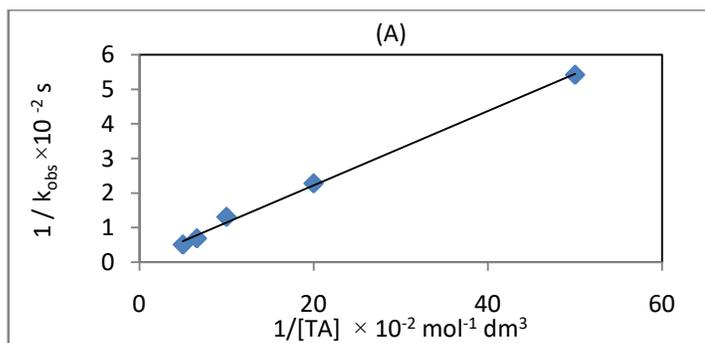


Fig.5(A)

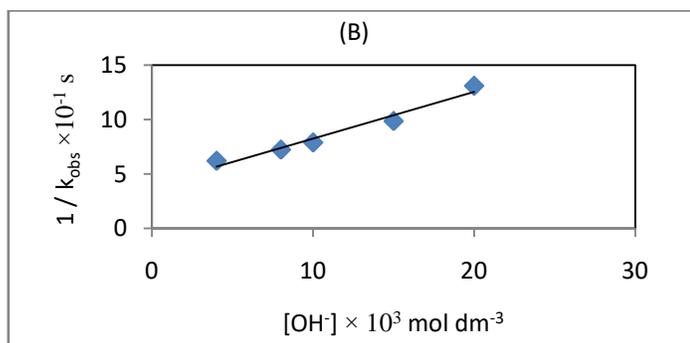


Fig.5(B)

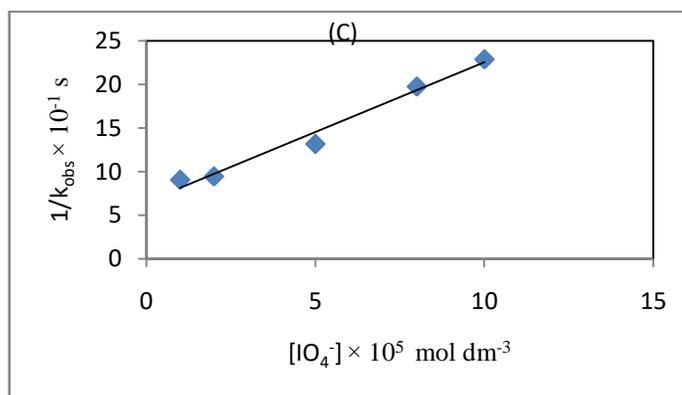


Fig.5(C)

**Table 1** Effect of variation of [DPC], [TA], [OH<sup>-</sup>] and [IO<sub>4</sub><sup>-</sup>] concentrations on the oxidation of TA by DPC in aqueous alkaline medium at 25°C and I=0.05mol dm<sup>-3</sup>

[DPC]×10 <sup>4</sup> (mol dm <sup>-3</sup> )	[TA]×10 <sup>3</sup> (mol dm <sup>-3</sup> )	[OH <sup>-</sup> ]×10 <sup>2</sup> (mol dm <sup>-3</sup> )	[IO <sub>4</sub> <sup>-</sup> ]×10 <sup>4</sup> (mol dm <sup>-3</sup> )	k <sub>obs</sub> ×10 <sup>2</sup> (S <sup>-1</sup> )
0.2	1.0	2.0	0.5	0.78
0.5	1.0	2.0	0.5	0.82
1.0	1.0	2.0	0.5	0.76
1.5	1.0	2.0	0.5	0.79
2.0	1.0	2.0	0.5	0.81
1.0	0.2	2.0	0.5	0.18
1.0	0.5	2.0	0.5	0.43
1.0	1.0	2.0	0.5	0.76
1.0	1.5	2.0	0.5	1.58
1.0	2.0	2.0	0.5	1.93
1.0	1.0	0.4	0.5	2.07
1.0	1.0	0.8	0.5	1.38
1.0	1.0	1.0	0.5	1.26
1.0	1.0	1.5	0.5	1.01
1.0	1.0	2.0	0.5	0.76
1.0	1.0	2.0	0.1	1.10
1.0	1.0	2.0	0.2	1.05
1.0	1.0	2.0	0.5	0.76
1.0	1.0	2.0	0.8	0.50
1.0	1.0	2.0	1.0	0.43

**Table. 2 (A):** Effect of temperature on the oxidation of tartaric acid by diperiodatocuprate(III) in an aqueous alkaline medium at [TA]= 1.0×10<sup>-3</sup> mol dm<sup>-3</sup>, [DPC] = 1.0×10<sup>-4</sup> mol dm<sup>-3</sup>, [OH<sup>-</sup>]=2.0×10<sup>-2</sup> mol dm<sup>-3</sup> [IO<sub>4</sub><sup>-</sup>] = 5.0×10<sup>-5</sup> mol dm<sup>-3</sup> and I= 0.05 mol dm<sup>-3</sup>.

Temperature(K)	k <sub>obs</sub> × 10 <sup>3</sup> (S <sup>-1</sup> )
293.15	6.94
298.15	7.62
303.15	9.93
308.15	13.12

**Table 2 (B).** Thermodynamic activation parameters for the oxidation of TA by DPC in aqueous alkaline medium and vanadium(V) in acidic medium [14].

Parameters	DPC	Vanadium(V)
Ea (kJ mol <sup>-1</sup> )	32 ± 3	77.1
ΔH <sup>#</sup> (kJ mol <sup>-1</sup> )	30 ± 2	74.6
ΔS <sup>#</sup> (JK <sup>-1</sup> mol <sup>-1</sup> )	-43 ± 3	-57.0
ΔG <sup>#</sup> (kJ mol <sup>-1</sup> )	179 ± 2	----
log A	3.8 ± 1	----