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RESEARCH ARTICLE

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Autocatalyzed oxidation of D-glucitol by alkaline copper (III) periodate complex: A kinetic and mechanistic approach

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Abstract

An autocatalyzed oxidation of D-glucitol (DG) by diperiodatocuprate (III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.06 mol dm^{-3} was studied spectrophotometrically. An autocatalysis was observed by one of the products formed, that is, Cu (II). A 1:2 stoichiometry (DG : DPC) exhibited reaction between the DG and DPC in an aqueous alkaline medium. The reaction was of first order in [DPC] when [DPC] < < [DG], while the order with respect to [DG] and [OH^-] was less than unity, whereas periodate had retarding effect on the rate of reaction. Ionic strength had a negligible effect on the rate of reaction. The main reaction products were identified by the spot tests and spectroscopic analysis. The product, Cu (II), catalyzed the reaction with a fractional order. A composite mechanism involving uncatalyzed and autocatalyzed reaction paths was proposed. The activation parameters with respect to slow step of the mechanism and also the thermodynamic quantities were determined and discussed.

KEYWORDS

autocatalysis, D-glucitol, diperiodatocuprate (III), kinetics, mechanism, oxidation

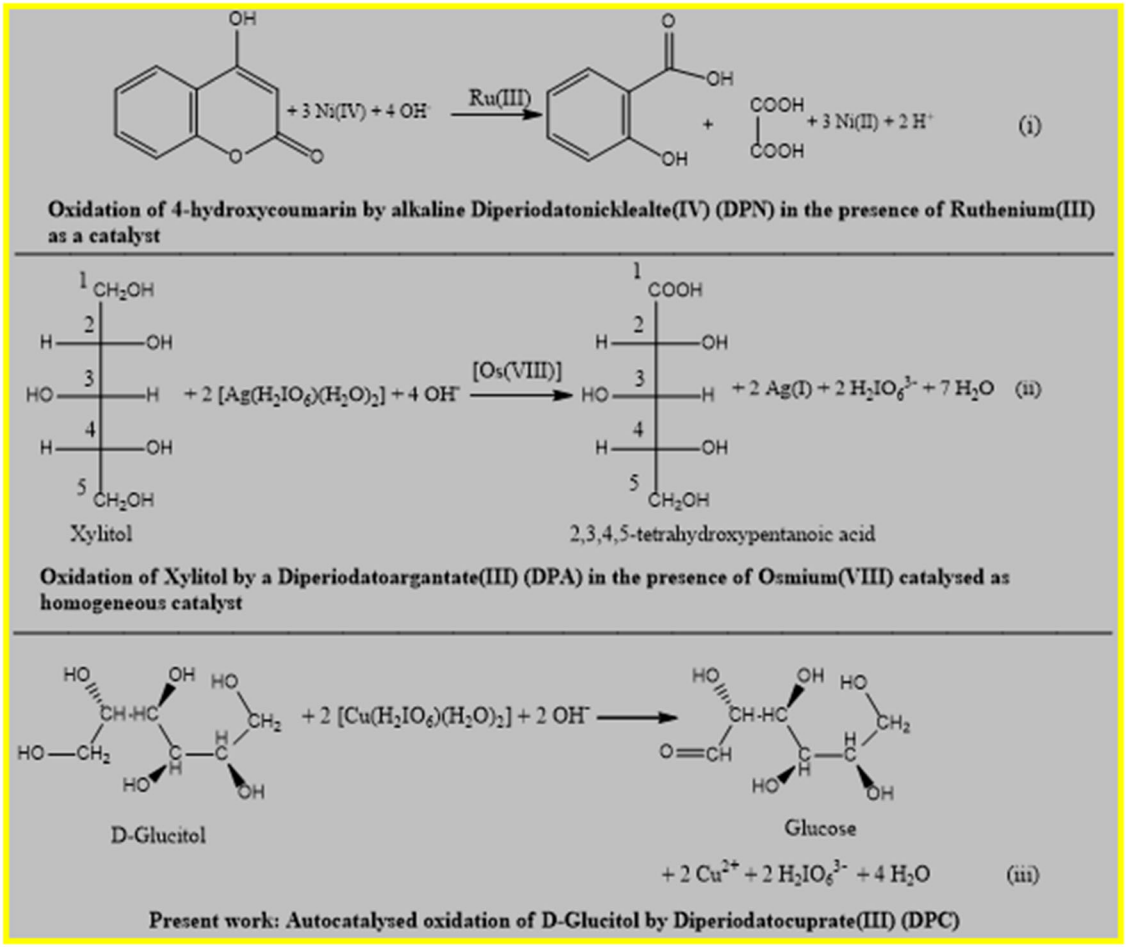
1 | INTRODUCTION

The study of the metals in their highest oxidation state has fascinated many researchers in the current years. Such transition metals can be stabilized by chelating with suitable bidentate or polydentate ligands. Metal chelate complexes have various of interactions that affect physical, chemical, and biological behavior. For example, Cu (II) and Zn (II) chelates influence the possible therapy for Alzheimer's disease, as copper and zinc are linked with the neurotoxicity of amyloid-beta peptide.[1–3]

Metal chelates such as diperiodatocuprate (III) (DPC),[4] diperiodatonickelate (IV) (DPN)[5] (reaction(i)), and diperiodatoargentate (III) (DPA)[6] (reaction (ii)) are good oxidants in alkaline medium as given below. And these are used for the analysis of several organic compounds.[7] The kinetics of self-decomposition of these complexes was studied in some details.[8] DPC is an excellent oxidant due to its restricted solubility and stability in aqueous medium. The reactivity of a few alcohols with DPC[9] is reported by Movius. The characterization, structural determination, and synthesis of DPC have been reported.[10] Copper periodate complexes in their +3 oxidation state have been widely used in the examination of several organic compounds.[11] The oxidation reactions by DPC studies are already under use[12] Complexes of copper have occupied a major role in the biochemistry.[13] In the copper (II) catalyzed oxidation of

various amino acids by peroxydisulfate involves copper (III) as an intermediate[14] compound. DPC is a versatile one-electron oxidant and involves multiple equilibria between different copper (III) species. Hence, it has intrigued many researchers to know as to which of the active species of the copper (III) is involved in the reaction.

by DPC, the present study has been taken up. The title reaction represents a full mechanistic and kinetic oxidation of DG by DPC in alkali media to establish the optimum conditions affecting such oxidation reaction as mentioned in reaction (iii), to understand more about the active species of the reactants in these media, and finally to determine the plausible oxidation mechanism on the



D-glucitol (DG) is a sugar alcohol having sweet taste, which is slowly metabolized in the human body. It can be obtained by changing the aldehyde group of glucose to a hydroxyl group. Prunes (cut portions) of apples, pears, and peaches contain most of the glucitol compounds.[15] It is converted to fructose by sorbitol-6-phosphate 2-dehydrogenase. DG is an isomer of mannitol, another sugar alcohol; the two differ only in the orientation of the hydroxyl group on β-carbon.[16]

In earlier report[17] on DPC oxidation, periodate and alkali had shown retarding effect; however, in the present study, we have obtained entirely different kinetic observations. Literature survey revealed that the mechanisms of autocatalysis are scanty.[18] In view of the observed study of autocatalysis by Cu (II) in the oxidation of DG basis of the observed kinetic and spectral studies were taken up. By understanding the mechanism, the reactivity of DG towards DPC was interpreted and understood.

2 | EXPERIMENTAL

2.1 | Materials and reagents

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of D-glucitol (Sigma-Aldrich) was prepared by dissolving an appropriate amount of recrystallized sample in double distilled water. The copper (III) periodate complex was prepared by standard procedure.[19] Existence of copper

(III) complex was verified by its UV-vis spectrum, which showed an absorption band with maximum absorption at 416 nm. The aqueous solution of copper (III) was standardized by iodometric titration and gravimetrically by the thiocyanate[20] method. The copper (II) solution was prepared by dissolving the known amount of copper sulfate (BDH) in distilled water. Periodate solution was prepared in hot water and used after keeping it for 24 h. Its concentration was ascertained iodometrically[21] at neutral pH by phosphate buffer. Because periodate is present in excess in DPC, the possibility of oxidation of DG by periodate in alkaline medium at 25°C was tested. The progress of the reaction was followed iodometrically. However, it was found that there was no significant reaction under the experimental conditions. KOH and KNO_3 were employed to maintain the required alkalinity and ionic strength respectively in reaction solutions.

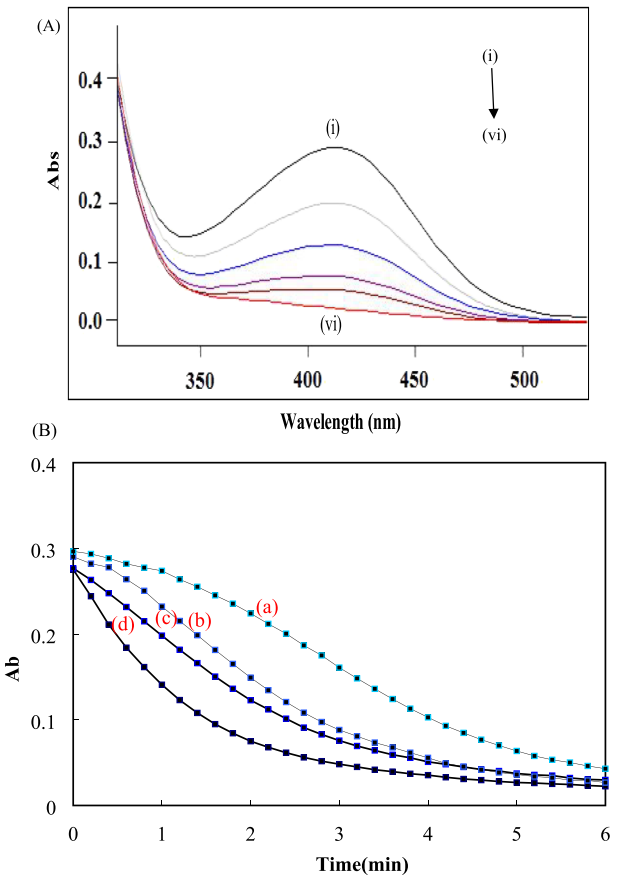


FIGURE 1 (A) Spectroscopic changes of diperiodatocuprate (III) (DPC) during the reaction period in the Cu (II) autocatalyzed oxidation of D-glucitol (DG) by DPC at 298 K (scanning interval 30 s). (B) Autocatalysis of Cu (II) on oxidation of DG by alkaline DPC at 298 K at various [Cu (II)] × 10^6 (a) 2, (b) 5, (c) 8, and (d) 10 mol dm^{-3}

2.2 | Kinetic measurements

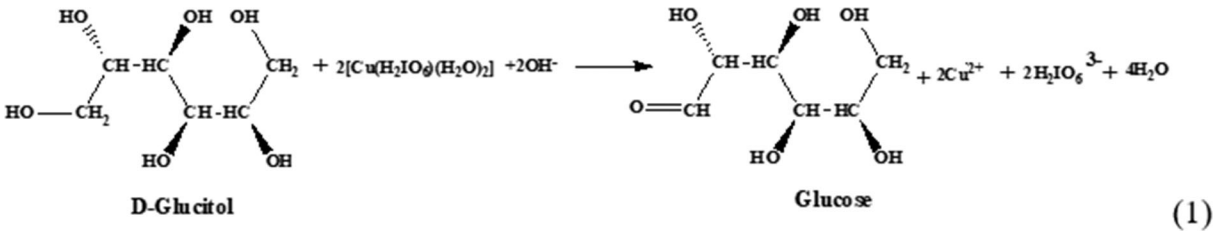
Kinetic measurements were carried out by using a Peltier accessory for temperature control attached to Varian CARY 50 Bio UV-vis Spectrophotometer connected with a rapid kinetic accessory (Varian, Victoria-3170, Australia). For pH measurement, an Elico pH meter model LI 120 was used. Kinetic runs were performed under pseudo-first order ([DG] > [DPC] at 25 ± 0.1°C) conditions. The required amount previously thermostat solution of DG and DPC was used to initiate the reaction, to which required concentrations of KNO_3, KOH, and KIO_4 were also added to maintain the conditions of the reaction. The progress of the reaction was studied spectrophotometrically at 416 nm, by recording the decrease in the absorbance due to DPC with the molar absorbancy index, ε = 6,231 ± 100 dm^3 mol^{-1} cm^{-1}. The negligible interference of other species present was observed in the reaction mixture at this wavelength. The log (Abs) versus time plots were used to calculate the pseudo-first-order rate constants, k_{obs}, and they were linear up to 30% completion of the reactions under the range of $[OH^-]$ used. Above 30% completion of the reaction, a nonlinearity was due to the autocatalysis, by copper (II) and the rate constants were reproducible about ±5%. During the kinetics, a constant (5.0 × 10^{-4} mol dm^{-3}) concentration of KIO_4 was used throughout the study unless otherwise stated.

The total $[OH^-]$ and $[IO_4^-]$ were calculated by the consideration of previously present ions in the DPC solution and that additionally added. No effect of added carbonate was observed on the rate of reaction. The spectral change of reaction progression has been shown in Figure 1A, in which decrease in [DPC] at 416 nm during the reaction was observed. The autocatalyzed oxidation of Cu (II) is also shown in Figure 1B. Microsoft 2007 Excel program was used for regression analysis of experimental data, standard deviation '*S*' and regression coefficient '*r*' of the points.

3 | RESULTS

3.1 | Stoichiometry and analysis of the product

Different sets of reaction mixtures containing varying ratios of DPC to DG in the presence of constant amount of OH^-, KNO_3, and KIO_4 were kept for 4 h in a closed vessel under nitrogen atmosphere. The unreacted DPC was estimated spectrophotometrically at 416 nm. The results indicated a 1:2 stoichiometry (DG : DPC) is as given in Equation (1).



(1)

The main reaction product was isolated by acidifying the reaction mixture followed by ether and ethyl acetate extraction. Each extract was dehydrated with anhydrous Na_2SO_4 and decanted; the solvent was removed by evaporation. The residue was recrystallized from warm glacial acetic acid. The main reaction product was identified as glucose that was confirmed by spot test and its molecular ion peak at 180 amu in ESI-Mass spectrum (Figure S1a), product also confirmed by ^{1}H-NMR spectrum (Figure S1b). Another product Cu (II) was identified by its UV-vis spectrum (Figure S1c). The reaction products did not undergo further oxidation under the present kinetic conditions.

3.2 | Reaction orders

The log k_{obs} versus log concentration plots were used to find the order of reaction with respect to [DG], [OH^-], and [IO_4^-]. These orders were obtained by varying the concentrations of DG, alkali, and periodate in turn while keeping all other concentrations and conditions constant.

3.3 | Effect of [DPC]

The concentration of DPC was varied in the range of 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3}, and the fairly constant

TABLE 1 Effects of [DPC], [DG], [OH], and [IO_4^-] on autocatalyzed oxidation of D-glucitol (DG) by diperiodatocuprate (III) (DPC) at 25°C, $I = 0.06$ mol dm^{-3}

[DPC] × 10^4 (mol dm^{-3})	[DG] × 10^3 (mol dm^{-3})	[IO_4^-] × 10^4 (mol dm^{-3})	[OH^-] × 10^2 (mol dm^{-3})	k_{obs} × 10^3 (s^{-1})	k_{cal} × 10^3 (s^{-1})
1.0	5.0	1.0	4.0	1.94	1.94
3.0	5.0	1.0	4.0	1.92	1.94
5.0	5.0	1.0	4.0	1.95	1.94
8.0	5.0	1.0	4.0	1.93	1.94
10.0	5.0	1.0	4.0	1.95	1.94
5.0	**3.0**	1.0	4.0	0.91	0.86
5.0	**4.0**	1.0	4.0	1.81	1.73
5.0	**5.0**	1.0	4.0	2.00	1.94
5.0	**6.0**	1.0	4.0	2.52	2.25
5.0	**8.0**	1.0	4.0	3.13	3.31
5.0	5.0	**0.5**	4.0	3.21	3.10
5.0	5.0	**0.8**	4.0	2.60	2.28
5.0	5.0	**1.0**	4.0	2.00	1.94
5.0	5.0	**3.0**	4.0	0.82	0.78
5.0	5.0	**5.0**	4.0	0.53	0.49
5.0	5.0	1.0	**0.5**	0.32	0.32
5.0	5.0	1.0	**1.0**	0.57	0.61
5.0	5.0	1.0	**2.0**	1.07	1.12
5.0	5.0	1.0	**4.0**	2.00	1.94
5.0	5.0	1.0	**6.0**	2.94	2.60

Bold Numbers indicates particular concentration was varied.

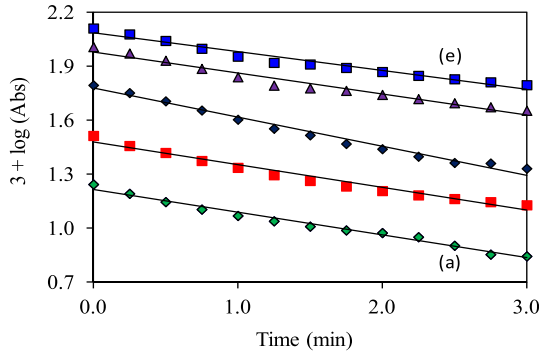


FIGURE 2 First order plots for the oxidation of D-glucitol (DG) by diperiodatocuprate (III) (DPC) in aqueous alkaline medium at 298 K. {[DPC] × 10^4 (mol dm^{-3}): (a) 0.1, (b) 0.3; (c) 0.5, (d) 0.8, and (e) 1.0}

k_{obs} values indicated that order with respect to [DPC] was unity (Table 1). This was also confirmed by linearity of the plots of log [Absorbance] versus time ($r \geq 0.956$, $S \leq 0.006$) up to 30% completion of the reaction (Figure 2).

3.4 | Effect of [D-glucitol]

The effect of DG on the rate of reaction was studied at constant concentrations of alkali, DPC, and periodate at a constant ionic strength of 0.06 mol dm^{-3}. The substrate, DG, was varied in the range of 3.0×10^{-3} to 8.0×10^{-3} mol dm^{-3}. The k_{obs} values were increased with an increase in the concentration of DG. The order with respect to [DG] was found to be less than unity (i.e., 0.22) (Table 1) ($r \geq 0.978$, $S \leq 0.003$).

3.5 | Effect of [alkali]

The effect of increase in concentration from 0.5×10^{-2} to 6.0×10^{-2} of alkali on the reaction was studied at constant concentrations of G-glucitol, DPC, and periodate at a constant ionic strength of 0.06 mol dm^{-3} at 298 K. The rate constants increased with increase in alkali concentrations (Table 1), indicating fractional order (i.e., 0.5) dependence of rate on alkali concentration ($r \geq 0.918$, $S \leq 0.008$).

3.6 | Effect of [periodate]

The effect of concentration of periodate was studied by varying the periodate concentration from 5.0×10^{-5} to 5.0×10^{-4} mol dm^{-3} keeping all other reactant concentrations constant. It was found that periodate had retarding effect on the rate of reaction. The order with respect to [periodate] was negative less than unity (i.e., −0.26) (Table 1) ($r \geq 0.901$, $S \leq 0.005$).

3.7 | Effect of ionic strength (*i*) and dielectric constant of the medium (*D*)

The addition of KNO_3 at constant [DPC], [G-glucitol], [OH^-], and [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 the *t*-butyl alcohol and water percentage. The *D* values were calculated using 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 total mixture. The decrease in dielectric constant of the reaction medium had no effect on the rate of reaction.

3.8 | Effect of initially added products

The initially added product, copper (II), was studied in the range 2.0×10^{-6} to 2.0×10^{-5} mol dm^{-3} when all other reactant concentrations were kept constant (Table 2). The initially added Cu (II) enhanced the rate of reaction with an order + 0.22 (Figure 3). However, the other product glucose did not have any significant effect on the rate of the reaction.

3.9 | The study of polymerization

The intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile monomer initially added, was kept

TABLE 2 Effects of added product [Cu (II)] on oxidation of D-glucitol (DG) by diperiodatocuprate (III) (DPC) at 298 K, $I = 0.06$ mol dm^{-3}

[Cu (II)] × 10^6 (mol dm^{-3})	$k_{obs} \times 10^3$ (s^{-1})
2.0	6.08
5.0	6.66
8.0	7.45
10	8.41
15	9.22
20	9.72

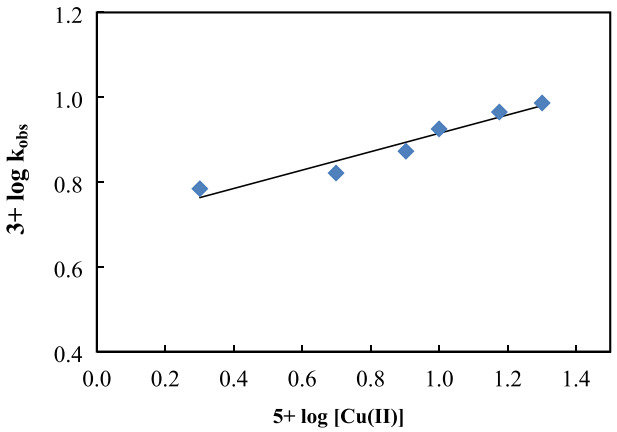


FIGURE 3 Order plot of 3 + log k_{obs} against 5 + log [Cu (II)]

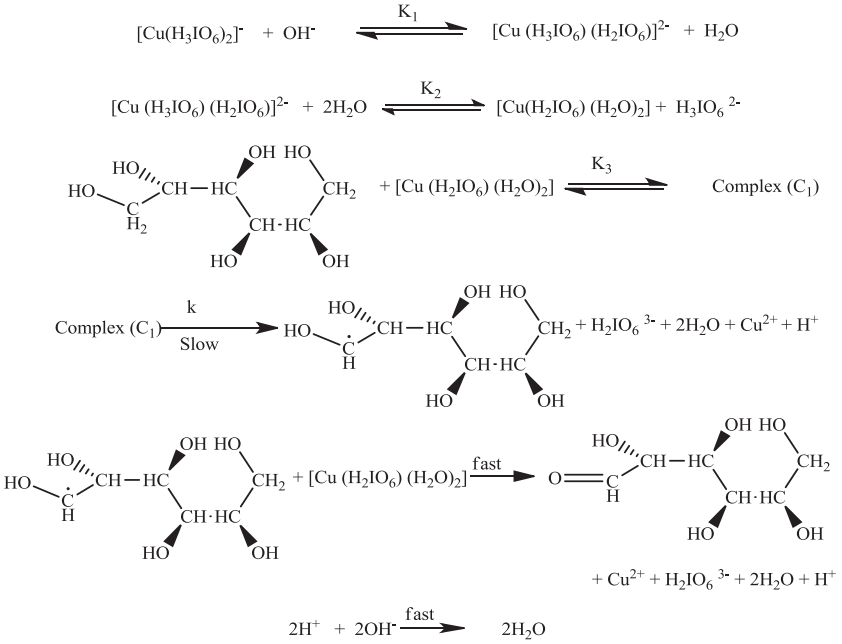
for 2 h in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either DPC or D-glucitol alone with acrylonitrile did not induce any polymerization under the same conditions as those induced for reaction mixture. Initially added acrylonitrile decreased the rate of reaction indicating free radical intervention, which is the case in the earlier work.[22] Such type of free radical intervention is observed in earlier works.[4,6]

3.10 | Effect of temperature (*T*)

The rate of reaction was measured for every 5 K raise in the temperature (298, 303, 308, 313/K) at varying [DG], [alkali], and [IO_4^-]. The rate constants were found to increase with the increase in temperature. The rate constants (k) of the slow step of Scheme 1 were obtained from the slopes and intercepts of $1/k_{obs}$ versus 1/[DG], $1/k_{obs}$ versus [$H_3IO_6^{2-}$], and $1/k_{obs}$ versus $1/[OH^-]$ plots at four different temperatures, and these were used to calculate the activation parameters (Table 3A). The energy of activation corresponding to these constants was evaluated from the Arrhenius plot of log k versus $1/T$ ($r \geq 0.9987$, $S \leq 0.011$), and other activation parameters obtained are tabulated in Table 3B.

4 | DISCUSSION

The $[Cu(HIO_6)_2(OH)_2]$[7–23] has been reported as water-soluble copper (III) periodate complex in an aqueous alkaline medium. However, studies at a higher pH range employed showed that periodate is unexpected to exist as HIO_6^{4-} (as present in the complex) as is clear from its involvement in the multiple equilibria[24] (Equations 2–4) depending upon pH of the solution. Periodic acid exists as $H_4IO_6^-$ at pH 7 and as H_5IO_6 in acid medium. Thus, in the present study in alkaline medium, $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ are found to be as main active species. Periodate dimerizes[4] at higher concentration. However, in the present kinetic conditions, the formation of this kind of species is negligible. Thus, [Cu (H_3IO_6) (H_2IO_6)]$^{2-}$ is the soluble copper (III) periodate complex in the employed pH conditions, also supported by the earlier work.[25]



SCHEME 1 Mechanism of oxidation of D-glucitol (DG) by diperiodatocuprate (III) (DPC)

$$H_5IO_6 \underset{}{\overset{K_1'}{\rightleftharpoons}} H_4IO_6^- + H^+ \qquad K_1' = 1.04\times 10^{-1} \qquad (2)$$

$$H_4IO_6^- \underset{}{\overset{K_2'}{\rightleftharpoons}} H_3IO_6^{2-} + H^+ \qquad K_2' = 3.80\times 10^{-8} \qquad (3)$$

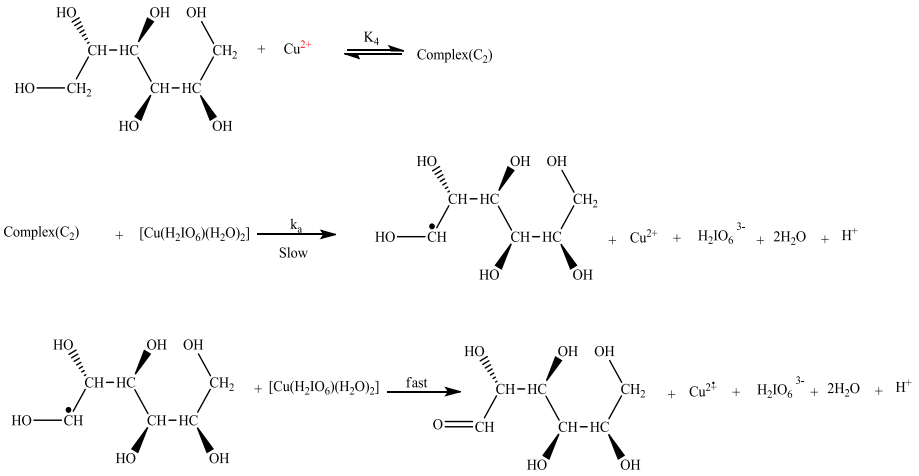
$$H_3IO_6^{2-} \underset{}{\overset{K_3'}{\rightleftharpoons}} H_2IO_6^{3-} + H^+ \qquad K_3' = 1.02\times 10^{-11} \qquad (4)$$

TABLE 3 Effects of temperature on Cu (II) autocatalyzed oxidation of D-glucitol (DG) by diperiodatocuprate (III) with respect to slow step of Scheme 1

Temperature (K)	$k \times 10^3$ (s^{-1})		
A			
298	1.13		
303	1.66		
308	2.05		
313	3.26		
B			
Parameters			
$\Delta H^{\#}$ (kJ mol^{-1})	64 ± 2		
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−60 ± 2		
$\Delta G^{\#}$ (kJ mol^{-1})	82 ± 1		
C			
Temperature (K)	$K_1 \times 10$ (dm^3 mol^{-1})	$K_2 \times 10^5$ (mol dm^{-3})	$K_3 \times 10^{-3}$ (dm^3 mol^{-1})
298	4.7 ± 0.2	5.7 ± 0.3	3.8 ± 0.1
303	6.5 ± 0.4	2.4 ± 0.06	6.0 ± 0.3
308	8.1 ± 0.6	1.8 ± 0.03	8.8 ± 0.4
313	11.1 ± 0.7	0.88 ± 0.02	9.9 ± 0.5
D			
Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3
ΔH (kJ mol^{-1})	45.4 ± 0.6	−91.4 ± 2.0	49.9 ± 0.7
ΔS (J K^{-1} mol^{-1})	166 ± 4	−390 ± 20	237 ± 15
ΔG_{298} (kJ mol^{-1})	−3.8 ± 0.1	24.2 ± 0.9	−20.4 ± 0.8

Note: (A) Effect of temperature; (B) activation parameters; (C) effect of temperature to calculate K_1, K_2, and K_3; and (D) thermodynamic quantities using K_1, K_2, and K_3.

The results obtained in the present study were entirely different from the earlier work on DPC oxidation.[26] Further kinetic studies were made in order to check the active species of DPC in such alkaline media. It was observed that the reaction exhibited an order of negative fraction with respect to [IO_4^-], less than unit order in DG and alkali concentrations (Table 1). In view of the retarding effect of periodate, the active species of DPC have been proposed as [$Cu(H_2IO_6)(H_2O)_2$], which was also observed in earlier report,[25] and the mechanism befitting the obtained results was proposed (Scheme 1).In aqueous alkaline medium, a diaquomonoperiodato copper (III) complex (MPC) (in Equation 5) was produced due to substitution of bidentate ligand [$H_3IO_6^{2-}$] of DPC



SCHEME 2 Mechanism of autocatalysis by Cu (II) in the oxidation of D-glucitol (DG) by diperiodatocuprate (III) (DPC)

by water molecules, and its formation was important in the present study. The kinetics and mechanistic study of oxidation by silver (III) and nickel (IV) periodate complexes[27,28] also reported the similar form of complexes.

$$[Cu(H_3IO_6)_2]^- + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Cu(H_2IO_6)(H_3IO_6)]^{2-} + H_2O \quad (5)$$

$$[Cu(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \underset{}{\overset{K_2}{\rightleftharpoons}} [Cu(H_2IO_6)(H_2O)_2] + H_3IO_6^{2-} \quad (6)$$

The inverse fractional order in $[IO_4^-]$ might be also due to this reason. Such types of equilibria have been well noticed in literature.[12] Also the spectra of Cu (III) periodate complex were dependent on $[OH^-]$, and the absorption becomes almost constant, indicating the predominance of one species, presumably $[Cu(H_2IO_6)(H_2O)_2]$. Because of this and the fact that rate is a function of $[OH^-]$ (less than unit order), the main oxidant species is $[Cu(H_2IO_6)(H_2O)_2]$, and its formation equilibrium (6) is important in the reaction. The less than unit order in [DG] presumably resulted from the formation of a complex (C_1) between the oxidant and DG prior to the formation of the products. K_3 is the composite equilibrium constant comprising the equilibrium to bind DG to MPC species to form a complex (C_1).[6] Then, this complex (C_1) decomposed in a slow step to form a free radical derived from DG. This free radical species further reacted with another molecule of MPC species in a fast step to yield the products such as D-glucose, Cu (II), and periodate. Similar type of reaction mechanism was observed in the earlier work.[6] On this basis, the detailed mechanistic pathway involving MPC species for the oxidation of DG is shown in Scheme 1:

The Michaelis–Menten plot proved the complex formation between DPC and DG, which explains the less than unit order dependence on [DG]. Such a complex between a substrate and an oxidant has been observed in other studies.[29]

$$\text{rate} = \frac{-d[DPC]}{dt} = \frac{kK_1K_2K_3[DG][OH^-][DPC]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[DG][OH^-]}$$
$$k_{obs} = \frac{\text{rate}}{[DPC]} = \frac{kK_1K_2K_3[DG][OH^-]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[DG][OH^-]}. \quad (7)$$

Scheme 1 leads to the rate law 7

The rate law 7 can be rearranged into the following form, which is suitable for verification.

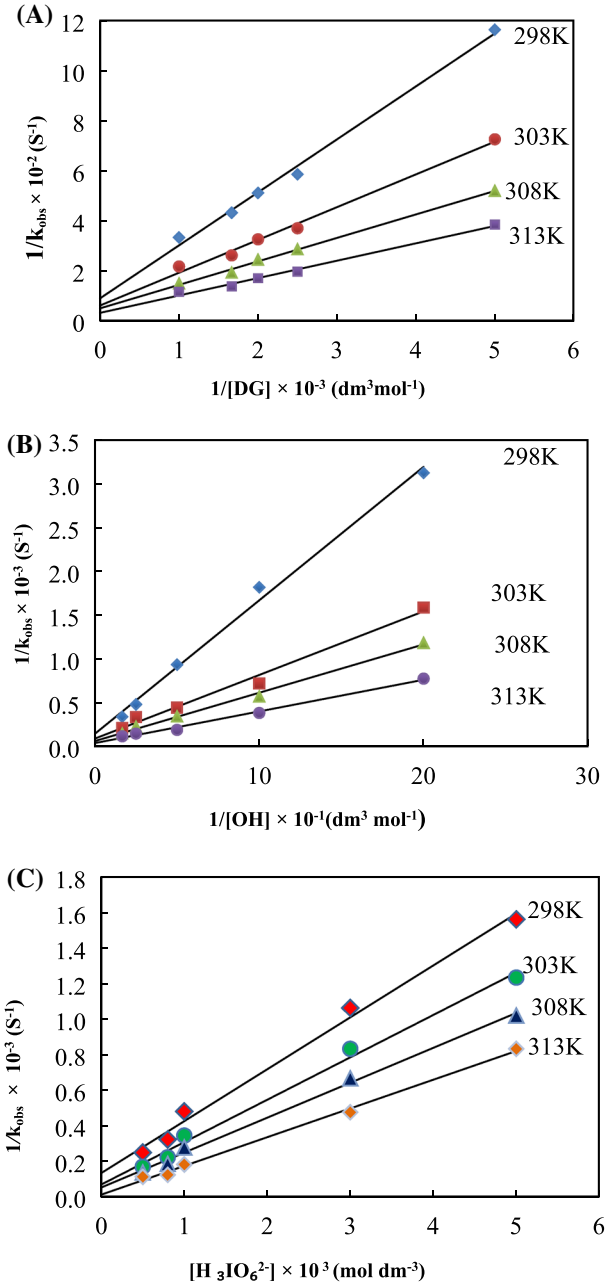


FIGURE 4 Verification of rate law 7 for the oxidation of DG by diperiodatocuprate (III) (DPC). Plots of (A) $1/k_{obs}$ versus 1/[DG], (B) $1/k_{obs}$ versus $1/[OH^-]$, (C) $1/k_{obs}$ versus $[H_3IO_6^{2-}]$, at four different temperatures (conditions as in Table 1). DG, D-glucitol

$$\frac{1}{k_{obs}} = \frac{[H_3IO_6^{2-}]}{kK_1K_2K_3[DG][OH^-]} + \frac{[H_3IO_6^{2-}]}{kK_2K_3[DG]} + \frac{1}{kK_3[DG]} + \frac{1}{k}. \quad (8)$$

According to Equation 8, other conditions being constant, plots of $1/k_{obs}$ versus $1/[OH^-]$($r \geq 0.9968$, $S \leq 0.014$), $1/k_{obs}$ versus 1/[DG] ($r \geq 0.9918$, $S \leq 0.016$), and $1/k_{obs}$ versus $[H_3IO_6^{2-}]$ ($r \geq 0.9989$, $S \leq 0.012$) should be linear and are found to be so (Figure 4). The slopes and intercepts of such plots lead to the values of K_1, K_2, K_3, and k as $(4.67 \pm 0.2) \times 10^{-1}$ mol dm^{-3}, $(5.7 \pm 0.3) \times 10^{-5}$ mol dm^{-3}, $(3.8 \pm 0.1) \times 10^{-3}$ dm^{-3} mol^{-1} and $(1.7 \pm 0.1) \times 10^{-2}$ s^{-1}, respectively. The equilibrium constant K_1 was far greater than K_2. This may be attributed to the greater tendency of DPC to undergo hydrolysis compared with the dissociation of hydrolyzed species in alkaline medium. Using these constants, the rate constants under varying conditions were calculated and compared with observed rate constants. There was a reasonable agreement between them (Table 1), which fortifies the proposed mechanism.

The negligible effect of ionic strength and dielectric constant of medium on the rate explains qualitatively the reaction between neutral and negatively charged ions, as seen in Scheme 1.

The thermodynamic quantities for the first, second, and third equilibrium steps of Scheme 1 were evaluated as follows. The $[H_3IO_6^{2-}]$, [DG] and $[OH^-]$ (as in Table 1) were varied at four different temperatures. The plots of $1/k_{obs}$ versus $1/[OH^-]$, $1/k_{obs}$ versus 1/[DG], and $1/k_{obs}$ versus $[H_2IO_6^{3-}]$ should be linear (Figure 4). From the slopes and intercepts, the values of K_1 were calculated at different temperatures, and these values are given in Table 3C. A van't Hoff's plot was made for variation of K_1 with temperature (log K_1 vs. $1/T$ ($r \geq 0.9624$, $S \leq 0.006$), and the values of enthalpy of reaction ΔH, entropy of reaction ΔS, and free energy of reaction ΔG were calculated for the first equilibrium step. These values are given in Table 3D. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before rate determining step is fairly fast and involves low activation energy.[30] In the same manner, K_2 and K_3 values were calculated at different temperatures, and their corresponding values of the thermodynamic quantities are given in the Table 3D.

The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favorable for electron transfer processes; the negative value of $\Delta S^{\#}$ indicates that the complex (C_1) is more ordered than the reactants.[31] The observed modest activation energy and sizeable entropy of activation supports, a complex state of transition in the reaction.[32] Because Scheme 1 is in accordance with the generally well-accepted principle of noncomplementary 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 earlier work.[32,33] The independence of rate of reaction on ionic strength[4] and dielectric constant of the

medium was due to the involvement of neutral species in the rate determining step of Schemes 1 and 2.

5 | AUTOCATALYSIS

The autocatalysis by one of the products, Cu (II), is interesting. The first order in [DPC] and less than unity in [DG] are observed. The apparent less than unit order in Cu (II) ion may be attributed to complex formation between DG and Cu (II). The complex C_2 is then subsequently involved in the interaction with MPC. These steps are shown in Scheme 2, which will form a part of Scheme 1. The plot of $1/k_{obs}$ versus 1/[Cu (II)] was linear, and a hypsochromic shift of Cu (II) from 765 to 757 nm in the presence of DG is the confirmation for complex formation between DG and Cu (II).

The rate law for autocatalyzed oxidation of DG by DPC is given by Equation 9

$$\text{rate} = \frac{k_a K_4 [DG][DPC]\left[Cu^{2+}\right]}{\left(1 + K_4\left[Cu^{2+}\right]\right)\left(1 + K_4[DG]\right)}, \quad (9)$$

or

$$k_{auto} = \frac{\text{rate}}{[DPC]} = \frac{k_a K_4 [DG]\left[Cu^{2+}\right]}{1 + K_4^2\left[Cu^{2+}\right][DG] + K_4\left[Cu^{2+}\right] + K_4[DG]}. \quad (10)$$

Thus, when $[Cu^{2+}]$ is initially present, a composite scheme involving steps of Schemes 1 and 2 operates

$$k_{gross} = k_{obs} + k_{auto}\ k_{gross} = \frac{k K_1 K_2 K_3 [DG][OH^-]}{\left[H_3IO_6^{2-}\right] + K_1[OH^-]\left[H_3IO_6^{2-}\right] + K_1K_2[OH^-] + K_1K_2K_3[DG][OH^-]} + \frac{k_a K_4 [DG]_T\left[Cu^{2+}\right]_T}{1 + K_4^2\left[Cu^{2+}\right][DG] + K_4\left[Cu^{2+}\right] + K_4[DG]}. \quad (11)$$

On rearranging k_{auto} part of Equation 11, we get,

$$\frac{[DG]}{k_{auto}} = \frac{1}{k_a K_4\left[Cu^{2+}\right]} + \frac{[DG]}{k_a\left[Cu^{2+}\right]} + \frac{1}{k_a} + \frac{K_4[DG]}{k_a}. \quad (12)$$

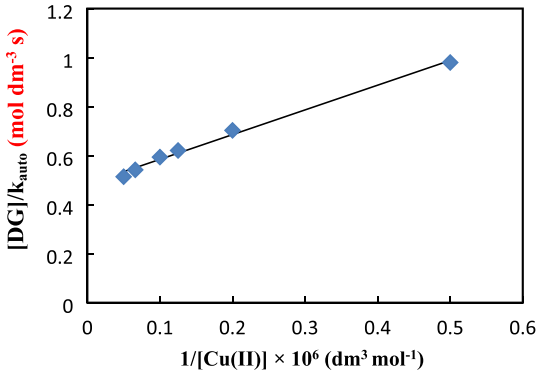


FIGURE 5 The plot of $[DG]/k_{auto}$ versus 1/[Cu (II)]. DG, D-glucitol

According to Equation 12, the plot of $[DG]/k_{auto}$ versus 1/[Cu (II)] should be linear ($R^2 > 0.992$, $S<0.0219$) and is found to be so (Figure 5). The slope and intercept of such plot lead to the values of K_4 and k_a as 5.023×10^5 dm^3 mol^{-1} and 10.1×10^2 dm^3 mol^{-1} s^{-1}, respectively.

6 | CONCLUSIONS

Among the various species of DPC, monoperiodatocuprate (III) (MPC), $[Cu(H_2IO_6)(H_2O)_2]$ is considered as active species among various species of DPC for the title reaction. The results demonstrate that in carrying out this reaction, the role of pH in the reaction medium is crucial. Autocatalysis by one of the products, Cu (II) is observed, and a composite rate law is obtained. Rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated, and activation parameters with respect to slow step of reaction are computed. The overall mechanistic sequence described here is consistent with product studies and kinetic studies.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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