Kinetic and Mechanistic Investigations of Oxidation of Myo-Inositol by Diperiodatocuprate(III) in Aqueous Alkaline Medium

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Abstract: The kinetics of oxidation of myo-inositol (INOS) by diperiodatocuprate(III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.07 mol/dm^3 was studied spectrophotometrically. The reaction between DPC and INOS in alkaline medium exhibits 1:1 stoichiometry. The reaction is of first order in DPC and less than unit order in INOS. The rate constants increase with increase in alkali concentration. Periodate has retarding effect on the rate of reaction. The reaction rate decreases with increase in ionic strength and decrease in dielectric constant of the medium. The main products were identified by spot test and spectral studies. A suitable mechanism was proposed on the basis of experimental results. The reaction constants involved in the different steps of the reaction mechanism were calculated. The activation parameters with respect to the slow step of the mechanism were determined.

Keywords: Diperiodatocuprate(III), Kinetics, Myo-inositol, Oxidation

Introduction

Myo-inositol is a water soluble six membered cyclic polyol, which is snthesised by both eukaryotes and prokaryote[1]. In humans most inositol is sythesised to an extent of few grams per day[2] in the kidneys. Myo-inositol and some of its mono and polyphosphates function as the basis for a number of signaling and secondary messenger molecules. These are involved in insulin signal transduction[3], gene expression[4,5] breakdown of fats and reducing blood cholesterol[6], phosphorus storage[7,8] and oligosaccharide synthesis[9] .

Oxidation of myo-inositol was studied by different oxidants like alkaline potassium periodate[10], alkaline hexacyano ferrate(III) ion in presence of Os^{VIII}, V^{V} in acid medium[11] in absence[12] and presence[13] of Cu^{II}, periodic acid[14,15]. The literature survey reveals that there are no reports on the mechanistic studies of myo-inositol oxidation by DPC in alkaline medium. The title reaction was studied to investigate the redox chemistry of Cu^{III} in aqueous alkaline medium and to arrive plausible mechanism.

Experimental

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of INOS (Merk) was prepared by dissolving an appropriate amount of recrystallized sample was prepared in double distilled water. The copper(III) periodate complex was prepared[16] and standardized by the standard procedure[17a]. All other reagents, namely KOH, KNO$_3$, CuSO$_4$ and KIO$_4$ were of analar grade.

Kinetic measurements

Kinetic measurements were performed by monitoring absorbance changes using a spectrophotometer with fully thermostated cell compartment. All kinetic measurements were performed in glass stoppered Pyrex boiling tubes coated black to eliminate photochemical effects. The reactions were carried out under pseudo-first order conditions by taking a known excess of INOS over DPC at 301 K. Appropriate amounts of INOS, KOH, KNO$_3$ and water to keep the total volume constant were equilibrated at constant temperature (± 0.1 ^{o}C). A measured amount of DPC solution also pre-equilibrated at the same temperature was rapidly added to the mixture. The progress of reaction was followed by measuring the absorbance of unreacted DPC in the reaction mixture present in 1 cm cell in a thermostated compartment of a Varian CARY 50 Bio UV-Vis spectrophotometer (Varian, Victoria – 3170, Austrilia) at 415 nm. It was verified that other constituents of the reaction mixture do not absorb significantly at this wavelength. The application of Beer's law to DPC at 415 nm had been verified and extinction coefficient, ϵ, was found to be 6250$\pm$50 dm^3 mol^{-1} cm^{-1}. The pseudo-first-order rate constants, k$_{obs}$ calculated from the linear plots of log[DPC] *versus* time were reproducible within $\pm 4\%$ and are average of at least three independent kinetic runs. The plots were linear over 85% completion of the reaction (Figure 1). Regression analysis of experimental data to obtain regression coefficient *r* and the standard deviation *S*, of points from the regression line, was performed with the Microsoft Excel programme.
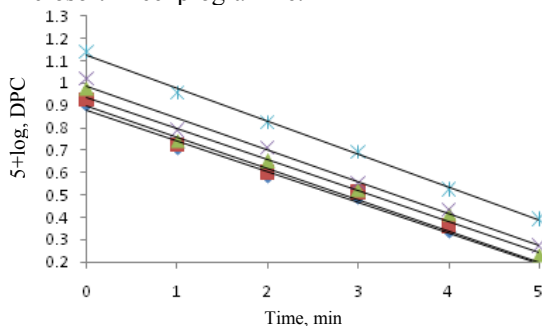
Figure 1. First order plots for the oxidation of inositol by diperiodatocuprate(III) in aqueous alkaline medium at 28 ^{o}C; [inositol] = 1 x 10^{-4} ; [OH$^-$] = 0.01M; *I* = 0.07mol dm^{-3}; [DPC] x 10^5 mol dm^{-3}: (1) 0.2 (2) 0.5 (3) 0.7 (4) 1.0 and (5) 2.0

## Results and Discussion

Stoichiometry and product analysis

Different sets of concentrations of reactants in 0.01 mol dm^{-3} KOH and at constant ionic strength, *I* = 0.07 mol dm^{-3} were kept in a closed container under nitrogen atmosphere at 28 ^{o}C. After one hour DPC concentration was assayed by measuring the absorbance at 415 nm. The results indicate that two moles of DPC reacts with one mole of inositol, as shown in equation (1). The main reaction products were identified as Cu^{II} and inosose.

The formation of Cu^{II} is identified by its color and inosose was tested spectrophotometrically by addition of 2, 4- dinitrophenylhydrazine to the reaction mixture, following a method described in the literature[17b]. The ketone was identified by the observation of two absorbance bands at 430 and 510 nm characteristic of the 2,4-dinitrophenylhydrazone derivative.

Reaction

$$C_6H_{12}O_6 + [Cu(OH)_2(H_3IO_6)]^- + 2OH^- \rightleftharpoons C_6H_{11}O_6 + Cu(OH)_2 + H_2IO_6^{3-} + 2H_2O$$
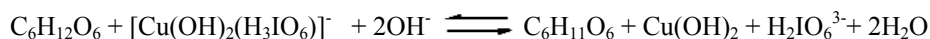
Reaction order

The orders were determined from the slopes of $logk_{obs}$ *versus* log[concentration] plots by varying the concentrations of inositol, KOH and KIO_4, in turn, while keeping others constant.

Effect of DPC

At constant concentrations of inositol, KOH and other conditions constant, the DPC concentration was varied between 2×10^{-6} to 2×10^{-5} mol dm^{-3}. The plot of log[DPC] *versus* time, was linear over more than three half lives of the reaction for different initial DPC concentration (Figure 1), which indicates the first order with respect to DPC concentration. This was also confirmed by the almost constant values of pseudo-first order rate constant, k_{obs} for different DPC concentration (Table 1).

Table 1. Effect of the variation of DPC, INOS, OH$^-$ and IO$_4^-$ concentrations on diperiodato-cuprate(III) oxidation of inositol in aqueous alkaline medium at 28 ^{0}C, $I = 0.07$ mol dm^{-3}

[DPC] 10^6 mol dm^{-3}	[INOS]10^4 mol dm^{-3}	[IO$_4^-$]10^6 mol dm^{-3}	[OH$^-$]10^2 mol dm^{-3}	k_{obs}x10^2 s^{-1}	k_{cal}x10^2 s^{-1}
2.0	1.0	2.0	1.0	18.23	18.20
5.0	1.0	2.0	1.0	18.23	18.20
7.0	1.0	2.0	1.0	18.23	18.20
10.0	1.0	2.0	1.0	18.23	18.20
20.0	1.0	2.0	1.0	18.23	18.20
7.0	0.2	2.0	1.0	6.00	5.98
7.0	0.5	2.0	1.0	12.04	12.05
7.0	1.0	2.0	1.0	18.23	18.20
7.0	1.5	2.0	1.0	21.78	21.78
7.0	2.0	2.0	1.0	24.45	24.44
7.0	1.0	2.0	1.0	18.23	18.20
7.0	1.0	5.0	1.0	17.58	17.60
7.0	1.0	7.0	1.0	17.23	17.25
7.0	1.0	10.0	1.0	16.74	16.73
7.0	1.0	20.0	1.0	15.20	15.19
7.0	1.0	2.0	0.002	1.75	1.74
7.0	1.0	2.0	0.02	9.40	9.42
7.0	1.0	2.0	0.2	16.91	16.92
7.0	1.0	2.0	1.0	18.23	18.20
7.0	1.0	2.0	2.0	18.36	18.37

Effect of inositol

The inositol concentration was varied in the concentration range 2×10^{-5} to 2×10^{-4} mol dm^{-3} at constant alkali, 0.01 mol dm^{-3}, constant ionic strength, 0.07 mol dm^{-3} and constant IO$_4^-$ concentration, 2×10^{-6}. As the inositol concentration increases the rate of reaction also increases (Table 1). The order with respect to inositol was found to be less than unity (Figure 2).

Effect of alkali and periodate

The effect of alkali concentration on the reaction was studied at constant concentrations of inositol and DPC at a constant ionic strength of 0.07 mol dm^{-3} at 28 ^{0}C. The rate constants increased with an increase in alkali concentration (Table 1). The order with respect to alkali was found to be less than unity (Figure 2). The effect of [IO$_4^-$] was observed by varying the concentration from 2×10^{-6} to 2×10^{-2} mol dm^{-3}, keeping all other reactants concentrations constant. It was found that the rate constants decreased with an increase in KIO$_4$ concentration (Table 1).
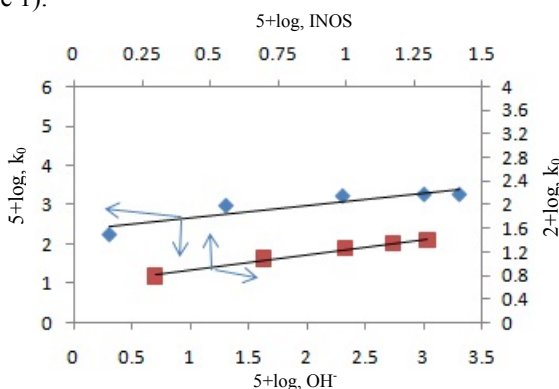
Figure 2. Order with respect to inositol and OH$^-$ ion concentrations on the oxidation of inositol by diperiodatocuprate(III) in aqueous alkaline medium at 301 K.(Conditions as in the Table 1)

Effect of ionic strength and dielectric constant

The effect of ionic strength was studied by varying the potassium nitrate concentration from 2×10^{-5} to 2×10^{-2} mol dm^{-3} at constant concentrations of DPC, inositol alkali and KIO$_4$. It was found that the rate constant decreased with increase in concentration of KNO$_3$ and the plot of logk$_{obs}$ *versus* $1/\sqrt{I}$ was linear ($r \geq 0.877$) with negative slope.

Dimethyl sulphoxide (DMSO) is a dipolar aprotic solvent and it has a dielectric constant less than that of water. To find out the effect of dielectric constant (D) on the rate of oxidation in aqueous alkaline medium, the reactions have been carried out at various proportions of DMSO in the medium. The D values were calculated from the equation $D = D_W V_W + D_D V_D$, where D_w and D_D are dielectric constants of pure water and DMSO respectively and V_w and V_D are the volume fractions of components of water and DMSO respectively in the total mixture. With an increase in the percentage of DMSO, the rate of the reaction decreased. In other words, the decrease in dielectric constant of the reaction medium had retarded the rate of reaction. It appears that the reaction is between negative ion and a dipole[9]. Hence, in aqueous alkaline medium, the reaction is between ion [Cu(OH)$_2$(H$_3$IO$_6$)]$^-$ and inositol molecule.

Effect of added product

The externally added product, Cu^{II} in the range 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} did not have any significant effect on the rate of the reaction.
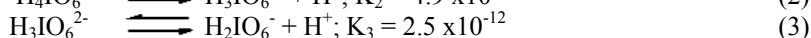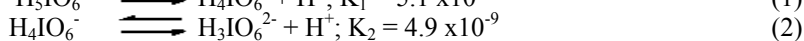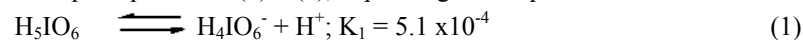
Polymerization study

To test the intervention of free radicals, the reaction mixture, to which a known quantity of acrylonitrile (scavenger) had been added initially, was kept for two hours under nitrogen atmosphere. On dilution with methanol, no precipitate of polymer was formed, indicating the absence of intervention of free radicals in the reaction.

Effect of temperature

The rate constants increased with an increase in temperature. The plot of lnk *versus* 1/T yield straight line and the values of activation parameters *viz*. enthalpy of activation ($\Delta H^{\#}$), entropy of activation($\Delta S^{\#}$) and Gibb's free energy ($\Delta G^{\#}$) are evaluated from the slope of the plot by using the Eyring equation[18,19] and are tabulated (Table 2).

Discussion

The water soluble copper(III) periodate complex was reported[20] to be $[Cu(HIO_6)_2(OH)_2]^{7-}$. However, in an aqueous alkaline medium and at a high pH range employed in the study, periodate is unlikely to exist as HIO_6^{4-}(as is present in the complex) as is evident from its involvement in the multiple equilibria[21] (1) – (3), depending on the pH of the solution

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+; K_1 = 5.1 \times 10^{-4} \qquad (1)$$
$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+; K_2 = 4.9 \times 10^{-9} \qquad (2)$$
$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^- + H^+; K_3 = 2.5 \times 10^{-12} \qquad (3)$$

Periodic acid exists as H_5IO_6 in acid medium and as $H_4IO_6^-$ near pH 7. Hence, under alkaline conditions as employed in this study the main species are expected to be H_3IO^{2-} and $H_2IO_6^{3-}$. Thus at the pH employed in this study the soluble copper(III) periodate complex might be $[Cu(OH)_2(H_3IO_6)_2]^{3-}$ a conclusion also supported by earlier work[22,23].

In most of the reports[24] on DPC oxidation, both OH$^-$ and periodate retarding effect on the rate of reaction. However, in the present kinetic study, different kinetic results have been obtained. In this study periodate had a retarding effect and OH$^-$ had an increasing effect on the rate of reaction (Table 1). The result of increase in rate of reaction with increase in alkalinity can be explained in terms of prevailing equilibrium of formation in terms of $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$ from $[Cu(OH)_2(H_3IO_6)_2]^{3-}$ and OH$^-$ as given in the following equation (4)

$$[Cu(OH)_2(H_3IO_6)_2]^{3-} + OH^- \xrightarrow{K_4} [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + H_2O \quad (4)$$

Also decrease in the rate with increase in $[H_3IO_6^{2-}]$ (Table 1) suggest that equilibrium of copper(III) periodate complex to form monoperiodatocuprate(III) (MPC) species as given in equation (5) is established.

$$[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{-4} \xrightarrow{K_5} [Cu(OH)_2(H_3IO_6)]^- + H_3IO_6^{2-} \quad (5)$$
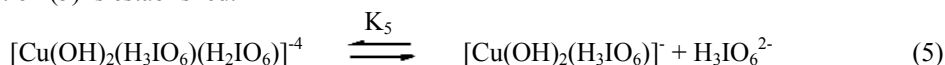
Such type of equilibria (4) and (5) have been well noticed in literature[25]. It may be expected that a lower periodate complex such as monoperiodatocuprate(III) (MPC) is more important in the reaction than the DPC. The inverse fractional order in $[H_3IO_6^{2-}]$ might also be due to this reason. Therefore, MPC might be the main reactive form of the oxidant.

The less than unit order in inositol presumably results from formation of a complex, C (green colour), between the MPC species and inositol prior to the formation of the products. K_6 is the composite equilibrium constant comprising the equilibrium to bind active species, MPC to inositol species to form a complex, C. The formation of complex was proved kinetically by Michaelis – Menten plot *i.e.*, a non zero intercept of the plot $1/k_{obs}$ *vs*. $1/[INOS]$ (Figure 3). The evidence for complex formation was also obtained in aqueous alkaline media from the UV–Vis spectrum of both DPC and inositol and DPC-inositol mixtures in which a bathochromic shift of 5nm from 271nm to 276 nm and hyperchromicity at 278 nm was observed. The complex formation between oxidant and substrate was also observed in literature[26]. This complex, C, undergoes decomposition in a slow step to give the final products inosose, Cu^{II} and periodate. From Scheme 1, the rate law (11) can be derived as follows;

$$\text{Rate} = -\frac{d[DPC)]}{dt} = k[C]$$

$$\text{Rate} = \frac{kK_4K_5K_6\,[INOS]\,[DPC]\,[OH^-]}{[H_3IO_6^{2-}]} \qquad (6)$$

$$[DPC]_T = [DPC]_f + [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + [Cu(OH)_2(H_3IO_6)]^- + [\text{complex, C}]$$

$$[DPC]_T = [DPC]_f + K_4[DPC]\,[OH^-] + \frac{K_4K_5[DPC][OH^-]}{[H_3IO_6^{2-}]} + \frac{K_4K_5K_6[DPC][OH^-][INOS]}{[H_3IO_6^{2-}]}$$

$$[DPC]_T = [DPC]_f \left\{ 1 + K_4[OH^-] + \frac{K_4K_5[OH^-]}{[H_3IO_6^{2-}]} + \frac{K_4K_5K_6[OH^-][INOS]}{[H_3IO_6^{2-}]} \right\}$$

$$[DPC]_f = \frac{[DPC]_T\,[H_3IO_6^{2-}]}{[H_3IO_6^{2-}] + K_4\,[H_3IO_6^{2-}]\,[OH^-] + K_4K_5[OH^-] + K_4K_5K_6[OH^-][INOS]} \qquad (7)$$

Where, T and f refer to total and free concentrations.

Similarly,

$$[INOS]_T = [INOS]_f + [\text{complex, C}]$$

$$[INOS]_f = \frac{[INOS]_T\,[H_3IO_6^{2-}]}{[H_3IO_6^{2-}] + K_4K_5K_6[OH^-][DPC]}$$

In view of low concentration of DPC used, the term $K_4K_5K_6[OH^-][DPC]$ can be neglected. Hence,

$$[INOS]_f = [INOS]_T \qquad (8)$$

Similarly; $[OH^-]_f = [OH^-]_T$ $\qquad (9)$

Substituting (2), (3) and (4) in (1) and omitting the subscripts T and f, we get,

$$\text{Rate} = -\frac{d[DPC]}{dt} = \frac{kK_4K_5K_6[DPC][INOS][OH^-]}{[H_3IO_6^{2-}] + K_4\,[H_3IO_6^{2-}]\,[OH^-] + K_4K_5[OH^-] + K_4K_5K_6[OH^-][INOS]}$$

$$k_{obs} = \frac{\text{Rate}}{[DPC]} = \frac{kK_4K_5K_6\,[INOS][OH^-]}{[H_3IO_6^{2-}] + K_4\,[H_3IO_6^{2-}]\,[OH^-] + K_4K_5[OH^-] + K_4K_5K_6[OH^-][INOS]} \qquad (10)$$

The rate law, (10) can be rearranged in to the following form, which is suitable for verification.

$$\frac{1}{k_{obs}} = \frac{[H_3IO_6^{2-}]}{k\,K_4K_5K_6[OH^-][INOS]} + \frac{[H_3IO_6^{2-}]}{kK_4K_5\,[INOS]} + \frac{1}{kK_6[INOS]} + \frac{1}{k} \qquad (11)$$

According to Eq. (11), other conditions being constant, plots of $1/k_{obs}$ *versus* $1/[OH^-]$ ($r \geq$ 0.998 , $S \leq 0.012$), $1/k_{obs}$ *versus* $1/[INOS]$ ($r \geq 0.998$, $S \leq 0.012$) and $1/k_{obs}$ *versus* $[H_3IO_6^{2-}]$

($r \geq 0.988$, $S \leq 0.027$) should be linear and are to be so (Figure 3). The slopes and intercepts of such plots lead to the values of K_4, K_5, K_6 and k as (15.6 ± 0.3) dm^3 mol^{-1},$(3.3\pm0.1 \times 10^{-4})$ mol dm^{-3}, $(1.0\pm0.03 \times 10^4)$ dm^3 mol^{-1} and (0.3722 ± 0.2) mol dm^{-3}s^{-1} , respectively. The value of K_4 and K_5 are in good agreement with earlier work[27]. These constants were used to calculate the rate constants over different experimental conditions; when compared with the experimental k_{obs} values, they were found to be in reasonable agreement with each other, which fortifies Scheme 1.
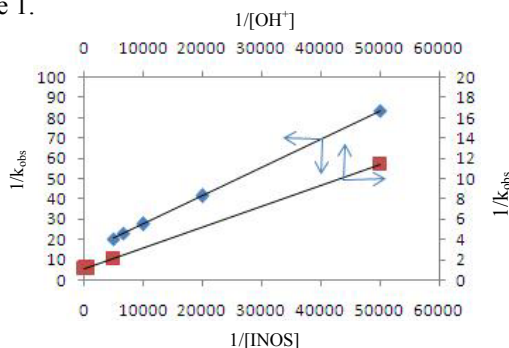
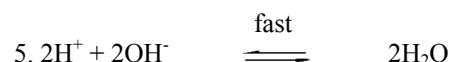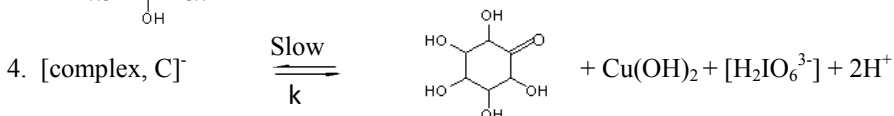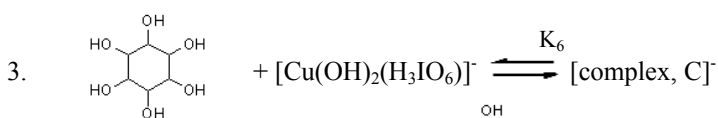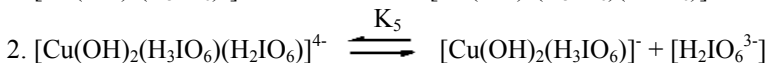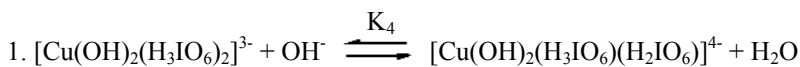**Figure 3.** Verification of rate law (11) for the oxidation of inositol by diperiodatocuprate(III) in aqueous alkaline medium at 301K.

The effect of ionic strength and dielectric constant of the medium on the rate explains quantitatively the reaction between molecule and ion, as seen in Scheme 1. The moderate $\Delta H^{\#}$ and $\Delta S^{\#}$ values (Table 2) are favorable for electron transfer reaction. The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants[28]. The observed modest enthalpy of activation and a higher rate constant for the slow step indicate that the oxidation presumably occurs via an inner sphere mechanism. This conclusion is supported by earlier observations[29].

Table 2. Arrhenius parameter for inositol oxidation by DPC in aqueous alkaline medium at 28 ^{0}C

$\Delta E^{\#}$ kJ/mol	$\Delta H^{\#}$ kJ/mol	$\Delta S^{\#}$ JK^{-1}mol^{-1}	logA	$\Delta G^{\#}$ kJ/mol
51.927	49.424	-62.43	7.7 ± 0.5	17.015

Mechanism

1. $[Cu(OH)_2(H_3IO_6)_2]^{3-} + OH^- \xrightleftharpoons{K_4} [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + H_2O$

2. $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} \xrightleftharpoons{K_5} [Cu(OH)_2(H_3IO_6)]^- + [H_2IO_6^{3-}]$

3. $+ [Cu(OH)_2(H_3IO_6)]^- \xrightleftharpoons{K_6}$ [complex, C]$^-$

4. [complex, C]$^-$ $\xrightleftharpoons{k}$ Slow $+ Cu(OH)_2 + [H_2IO_6^{3-}] + 2H^+$

5. $2H^+ + 2OH^- \xrightleftharpoons{\text{fast}} 2H_2O$

Conclusion

Among the various species of DPC in aqueous alkaline medium, $[Cu(OH)_2(H_3IO_6)]^-$ is considered as active species for the title reaction. The results indicated that in carrying out this reaction, the role of pH in the reaction medium is crucial. Rate constant of slow step and other equilibrium constants involved in the mechanism are 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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