Oxidation of Vanillin by Diperiodatocuprate(III) in Aqueous Alkaline Medium: A Kinetic and Mechanistic Study by Stopped Flow Technique

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ABSTRACT: The kinetics of oxidation of vanillin (VAN) by diperiodatocuprate(III) (DPC) in alkaline medium at a constant ionic strength of 0.50 mol dm^{-3} was studied spectrophotometrically. The reaction between DPC and vanillin in alkaline medium exhibits 1:2 stoichiometry (vanillin: DPC). The reaction is of first order in [DPC] and has less than unit order in both [VAN] and [alkali]. Intervention of free radicals was observed in the reaction. Increase in periodate concentration decreases the rate. The oxidation reaction in alkaline medium has been shown to proceed via a monoperiodatocuprate(III)–vanillin complex, which decomposes slowly in a rate-determining step followed by other fast steps to give the products. The main products were identified by spot test, IR, and MS studies. The reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed, and thermodynamic quantities are also determined.

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INTRODUCTION

In recent years, the study of the highest oxidation state of transition metals has intrigued many researchers. Transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands. Metal chelates such as diperiodatocuprate(III) [1] diperiodatoargentate(III) [2], and diperiodatonickelate(IV) [3] are good oxidants in a medium with an appropriate pH value. Copper(III) is shown to be an intermediate in the copper(II)-catalyzed oxidation of amino acids by peroxydisulfate [4]. The oxidation reaction usually involves the copper(II)–copper(I) couple, and such aspects are detailed in different reviews [5, 6]. The use of diperiodatocuprate(III) (DPC) as an oxidant in alkaline medium is new and restricted to a

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few cases because of its limited solubility and stability in aqueous medium. Copper complexes have occupied a major place in oxidation chemistry because of their abundance and relevance in biological chemistry [7–11]. Copper(III) is involved in many biological electron transfer reactions [12]. When the copper(III) periodate complex is oxidant and multiple equilibria between different copper(III) species [13] are involved, it would be interesting to know which of the species is the active oxidant.

3-Methoxy-4-hydroxy benzaldehyde, commercially called p-Vanillin and in general vanillin (VAN), occurs in nature as a glucoside, which hydrolyzes to vanillin and sugar. It is a very popular flavoring reagent in the food industry, and it is also useful in the synthesis of drugs. It is also used in the preparation of perfume and as a catalyst to polymerize methylacrylate [14]. Vanillin has both phenolic and aldehydic groups and is capable of undergoing three different types of reactions: those of aldehydic group, the phenolic hydroxyl, and aromatic nucleus. However, as a *p*-hydroxybenzaldehyde, vanillin does not undergo some very common aldehyde reactions, such as the Cannizzaro's reaction and the Benzoin condensation. If the hydroxyl group in vanillin is protected, it undergoes oxidation [15] to vanillic acid. As a phenol, vanillin forms esters and ethers, and the nucleus is easily substituted by halogen and nitro groups. In comparison with most other aldehydes, vanillin is notable for its stability. The kinetics of oxidation of vanillin by some oxidants is reported in the literature [16–19]. In view of this, we have undertaken the study of the oxidation of vanillin by diperiodatocuprate(III) in alkaline medium to understand the suitable mechanism and active species in such a medium.

EXPERIMENTAL

Materials and Reagents

All chemicals used were of reagent grade, and double distilled water was used throughout the work. A solution of vanillin (s.d-Fine, Mumbai, India) was prepared by dissolving an appropriate amount of recrystallized sample in double distilled water. The purity of vanillin sample was checked by comparing its IR spectrum with the literature data and with its mp 81–83°C. The required concentration of vanillin was prepared from its stock solution. The copper(III) periodate complex was prepared by standard procedure [20]. Existence of copper(III) complex was verified by its UV–Vis spectrum, which showed an absorption band with maximum absorption at 415 nm. The aqueous solution of copper(III) was standardized by iodometric titration and gravimetrically by the thiocyanate [21] method. The copper(II) and vanillic acid solutions were prepared by dissolving the known amount of copper sulfate (BDH, Mumbai, India) and vanillic acid crystals (s.d-Fine, Mumbai, India), respectively, in distilled water. Periodate solution was prepared by weighing the required amount of sample in hot water and used after keeping it for 24 h. Its concentration was ascertained iodometrically [22] at neutral pH by phosphate buffer. KOH and KNO_3 (BDH, AR, Mumbai, India) were employed to maintain the required alkalinity and ionic strength, respectively, in reaction solutions.

KINETIC MEASUREMENTS

The kinetic measurements were performed on a Hitachi 150-20 UV–Visible spectrophotometer attached to a rapid kinetic accessory (HI-TECH SFA-12). The kinetics was followed under pseudo-first-order condition, where [VAN] > [DPC] at 25 ± 0.1°C, unless specified. The reaction was initiated by mixing the DPC with VAN solution, which also contained the required concentration of KNO_3, KOH, and KIO_4, and the progress of the reaction was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC with the molar absorbancy index, ε to be 6230 ± 100 dm^3 mol^{-1} cm^{-1}. It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength.

The pseudo-first-order rate constants, k_{obs}, were determined from the log (absorbance) versus time plots. The plots were linear up to 85% completion of reaction under the range of [OH^-] used. The orders for various species were determined from the slopes of plots of log k_{obs} versus respective concentration of species except for [DPC] in which nonvariation of k_{obs} was observed as expected to the reaction condition. During the kinetics, a constant concentration viz. 1.0×10^{-4} mol dm^{-3} of KIO_4 was used throughout the study unless otherwise stated. Since periodate is present in the excess in DPC, the possibility of oxidation of vanillin 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 employed compared to the DPC oxidation of vanillin. The total concentration of periodate and OH^- was calculated by considering the amount present in the DPC solution and that additionally added. Kinetics runs were also

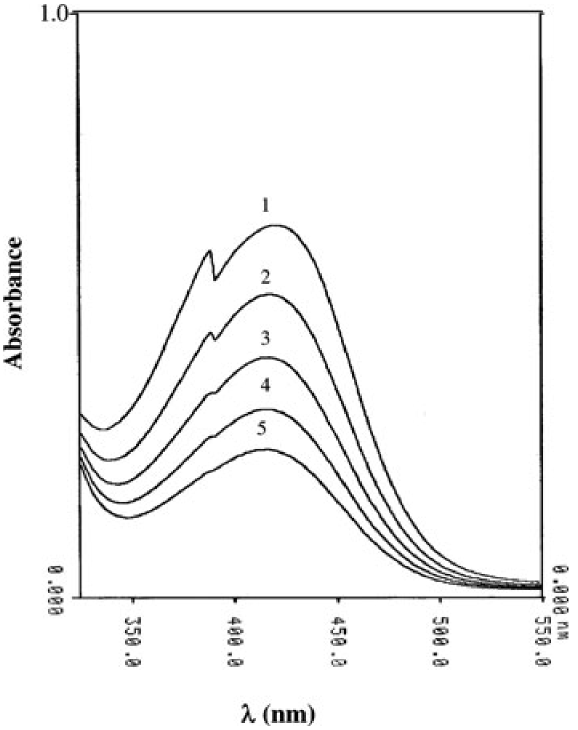


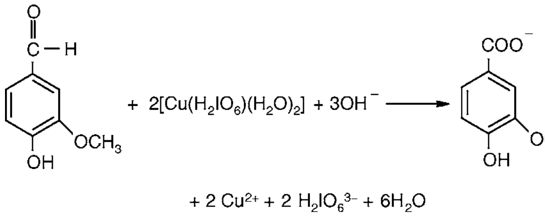
Figure 1 Spectroscopic changes occurring in the oxidation of vanillin by diperiodatocuprate(III) at 25°C, [DPC] = 1×10^{-4}, [VAN] = 1×10^{-3}, [OH^-] = 0.10, and $I = 0.50$ mol dm^{-3} with scanning time interval = 1 min.

carried out in N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates. The spectral changes during the reaction are shown in Fig. 1. It is evident from the figure that the concentration of DPC decreases at 415 nm. As shown in the figure, the small absorption peak at 390 nm could be due to charge transfer from oxygen to iodine, which disappears by time because of oxidative reaction.

RESULTS

Stoichiometry and Product Analysis

Different sets of reaction mixtures containing various ratios of DPC to vanillin in the presence of constant amounts of OH^- and KNO_3 were kept for 2 h in closed vessel under nitrogen atmosphere. The remaining concentration of DPC was estimated by spectrophotometrically at 415 nm. The results indicated 1:2 stoichiometry as given in Eq. (1).



(1)

The main 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 vanillic acid. The nature of vanillic acid was confirmed by its spot test [23] and also by IR spectrum (1686 cm^{-1} due to C=O stretching, 3486 cm^{-1} due to O—H stretching). It was confirmed by its melting point 206°C (literature mp 208°C). Further, vanillic acid was subjected to mass spectral analysis. MS data were obtained on a QP-5050A Shimadzu mass spectrometer using the EI ionization technique. The mass spectrum showed a molecular ion peak at 168 amu confirming vanillic acid. The product, Cu(II), was identified by UV–Vis spectra. The reaction products do not undergo further oxidation under the present kinetic conditions. Regression analysis of 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.

Reaction Orders

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

Effect of [Diperiodatocuprate(III)]

The oxidant DPC concentration was varied in the range 5.0×10^{-5} to 5.0×10^{-4} mol dm^{-3}, and the fairly constant k_{obs} values indicate that order with respect to [DPC] was unity (Table I). This was also confirmed by linearity of the plots of log [absorbance] versus time ($r \geq 0.986$, $S \leq 0.013$) up to 80% completion of the reaction (Fig. 2).

Table I Effect of [DPC], [VAN], [OH$^-$], and [IO$_4^-$] on Diperiodatocuprate(III) Oxidation of Vanillin in Alkaline Medium at 25°C, $I = 0.50$ mol dm^{-3}

[DPC] × 10^4 (mol dm^{-3})	[VAN] × 10^3 (mol dm^{-3})	[IO$_4^-$] × 10^4 (mol dm^{-3})	[OH$^-$] (mol dm^{-3})	k_{obs} × 10^2 (s^{-1})	
				Found	Calculated
0.5	1.0	1.0	0.1	1.20	1.21
0.8	1.0	1.0	0.1	1.19	1.20
1.0	1.0	1.0	0.1	1.20	1.24
2.0	1.0	1.0	0.1	1.18	1.20
3.0	1.0	1.0	0.1	1.20	1.20
1.0	0.5	1.0	0.1	0.68	0.71
1.0	0.8	1.0	0.1	0.99	1.04
1.0	1.0	1.0	0.1	1.20	1.24
1.0	3.0	1.0	0.1	2.31	2.45
1.0	5.0	1.0	0.1	3.13	3.04
1.0	1.0	1.0	0.05	0.89	0.87
1.0	1.0	1.0	0.08	1.09	1.12
1.0	1.0	1.0	0.1	1.20	1.24
1.0	1.0	1.0	0.3	1.78	1.73
1.0	1.0	1.0	0.5	1.93	1.88
1.0	1.0	0.1	0.1	2.79	2.84
1.0	1.0	0.3	0.1	2.19	2.21
1.0	1.0	0.5	0.1	1.79	1.81
1.0	1.0	0.8	0.1	1.41	1.42
1.0	1.0	1.0	0.1	1.20	1.24

Effect of [Vanillin]

The effect of vanillin on the rate of reaction was studied at constant concentrations of alkali, DPC, and periodate at a constant ionic strength of 0.50 mol dm^{-3}. The substrate, vanillin, was varied in the range 5.0 × 10^{-4} to 5.0 × 10^{-3} mol dm$^{-3.}$ The k_{obs} values increased with increase in concentration of vanillin. The order with respect to [vanillin] was found to be less than unity (Table I) ($r \geq 0.995$, $S \leq 0.007$).

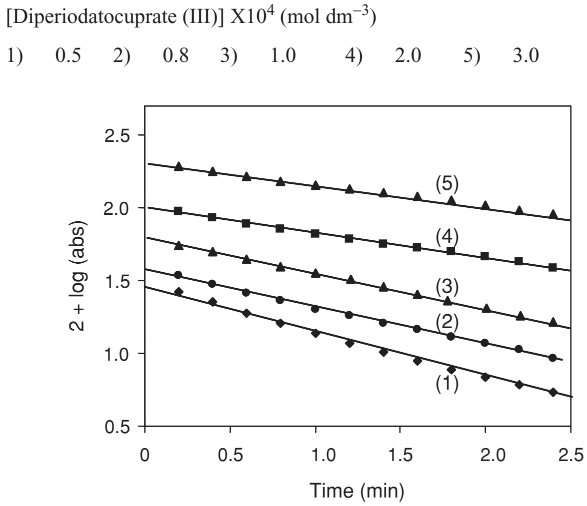


Figure 2 First-order plots on the oxidation of vanillin by diperiodatocuprate(III) in aqueous alkaline medium. [Diperiodatocuprate (III)] 1: 0.5 × 10^4 mol dm^{-3}, 2: 0.8 × 10^4 mol dm^{-3}, 3: 1.0 × 10^4 mol dm^{-3}, 4: 2.0 × 10^4 mol dm^{-3}, and 5: 3.0 × 10^4 mol dm^{-3}.

Effect of [Alkali]

The effect of increase in concentration of alkali on the reaction was studied at constant concentrations of vanillin, DPC, and periodate at a constant ionic strength of 0.50 mol dm^{-3} at 25°C. The rate constants increased with increase in alkali concentration (Table I), indicating fractional order dependence of rate on alkali concentration ($r \geq 0.998$, $S \leq 0.006$).

Effect of [Periodate]

The effect of increasing concentration of periodate was studied by varying the periodate concentration from 1.0 × 10^{-5} to 1.0 × 10^{-4} mol dm^{-3} keeping all other reactant concentrations constant. It was found that the added periodate had a retarding effect on the rate of reaction, the order with respect to periodate concentration being negative less than unity (Table I).

Effect of Ionic Strength (I) and Dielectric Constant on the Medium (D)

The addition of KNO_3 at constant [DPC], [VAN], [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 t-butyl alcohol and water percentage. 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 total mixture. The decrease in dielectric constant of the reaction medium has no effect on the rate of reaction.

Effect of Initially Added Products

The externally added products, vanillic acid and copper(II) ($CuSO_4$) 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

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 vanillin alone with acrylonitrile did not induce any polymerization under the same condition as those induced for reaction mixture. Initially, the added acrylonitrile decreases the rate of reaction indicating free-radical intervention, which is the case in earlier work [24].

Effect of Temperature (T)

The kinetics was studied at four different temperatures under varying concentrations of vanillin, alkali, and periodate, keeping other conditions constant. The rate constants were found to increase with 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/[VAN], $1/k_{obs}$ versus [$H_3IO_6^{2-}$], and $1/k_{obs}$ versus 1/[OH^-] plots at four different temperatures and were used to calculate the activation parameters. 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 II.

Table II Thermodynamic Activation Parameters for the Oxidation of Vanillin by DPC in Aqueous Alkaline Medium with Respect to the Slow Step of Scheme 1

(A) Effect of temperature

Temperature (K)	$k \times 10^2$ (s^{-1})
298	3.7
303	4.2
308	4.6
313	5.1

(B) Activation parameters (Scheme 1)

Parameters	Values
$\Delta H^{\#}$ (kJ mol^{-1})	13.1 ± 0.5
$\Delta S^{\#}$(JK^{-1} mol^{-1})	-227 ± 15
$\Delta G^{\#}$ (kJ mol^{-1})	81 ± 2

(C) Effect of temperature on equilibrium constants of Scheme 1
for the oxidation of vanillin by diperiodatocuprate(III) in alkaline medium

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	4.6 ± 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 using K_1, K_2, and K_3

Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3
ΔH (k J 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} (k J mol^{-1})	-3.8 ± 0.1	24.2 ± 0.9	-20.4 ± 0.8

DISCUSSION

The water-soluble copper(III) periodate complex is reported [25]to be $[Cu(HIO_6)_2]^{5-}$. However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as HIO_6^{4-}(as present in the complex) as is evident from its involvement in the multiple equilibria [26] ((2)–(4)) depending on the pH of the solution.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \tag{2}$$

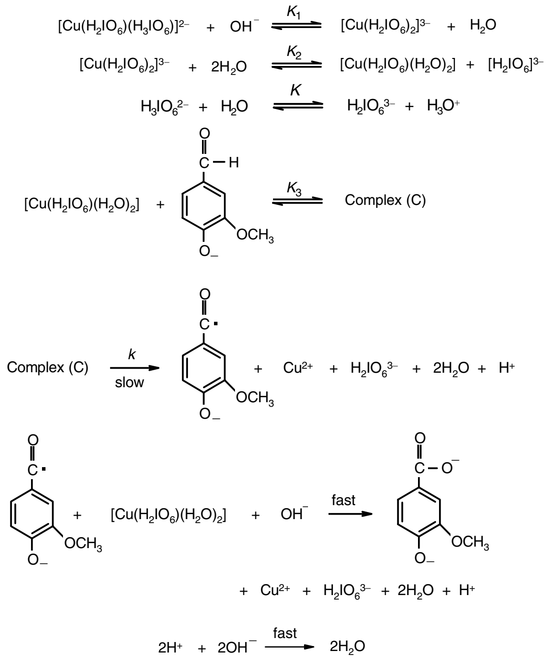
$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \tag{3}$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \tag{4}$$

Periodic acid exists in acid medium as H_5IO_6 and as $H_4IO_6^-$ around pH 7. Thus, under the conditions employed in alkaline medium, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerize [27]. 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), $[Cu(H_3IO_6)(H_2IO_6)]^{2-}$, a conclusion also supported by earlier work [28].

The reaction between the diperiodatocuprate(III) complex and vanillin in alkaline medium has the stoichiometry 1:2 (VAN:DPC) with a first-order dependence on [DPC] and an apparent order of less than unity in [substrate], [alkali] and negative fractional order dependence on the 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], $[OH^-]$, and $[IO_4^-]$ may be well accommodated. Lister [29] proposed three forms of copper(III) periodate in alkaline medium as diperiodatocuprate(III) (DPC), monoperiodatocuprate(III) (MPC), and tetrahydroxocuprate(III). The latter is ruled out as its equilibrium constant is 8.0×10^{-11} at 40°C. Hence, in the present study, DPC and MPC are to be considered as active forms of copper(III) periodate complex. It may be expected that a lower periodate complex such as MPC is more important in the reaction than the DPC. The results of increase in the rate with increase in alkali concentration and decrease in the rate with increase in periodate concentration suggest that equilibria of different copper(III) periodate complexes are possible as in Eqs. (5) and (6).

$$[Cu(H_2IO_6)(H_3IO_6)]^{2-} + OH^- \rightleftharpoons [Cu(H_2IO_6)_2]^{3-} + H_2O \tag{5}$$



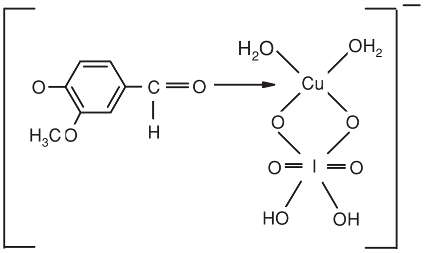
Scheme 1

$$[Cu(H_2IO_6)_2]^{3-} + 2H_2O \rightleftharpoons [Cu(H_2IO_6)(H_2O)_2] + [H_2IO_6]^{3-} \tag{6}$$

The inverse fractional order in $[IO_4^-]$ might also be due to this reason. Vanillin is known to exist as deprotonated form in alkaline medium because of its phenolic group. The less than unit order in [VAN] presumably results from formation of a complex (C) between the oxidant and vanillin prior to the formation of the products. K_3 is the composite equilibrium constant comprising the equilibrium to bind active species of vanillin to MPC species to form a complex (C). Then, this complex (C) decomposes in a slow step to form a free radical derived from vanillin. This free-radical species further reacts with another molecule of MPC species in a fast step to yield the products such as vanillic acid, Cu(II), and periodate.

So, the detailed mechanistic scheme for the oxidation of vanillin by diperiodatocuprate(III) is presented in Scheme 1.

The probable structure of the complex (C) is given by



Since 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 (as given in the Results section). This type of radical intermediate has also been observed in earlier work [30].

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV–Vis spectra of vanillin (1.0×10^{-3}), DPC (1.0×10^{-4}), $[\mathrm{OH^-}] = 0.1$ mol dm^{-3} and mixture of both. A bathochromic shift of about 7 nm from 342 to 349 nm in the spectra of DPC was observed. The Michaelis–Menten plot also proved the complex formation between DPC and vanillin, which explains the less than unit order dependence on [VAN]. Such a complex between a substrate and an oxidant has been observed in other studies [31].

Scheme 1 leads to the rate law (7)

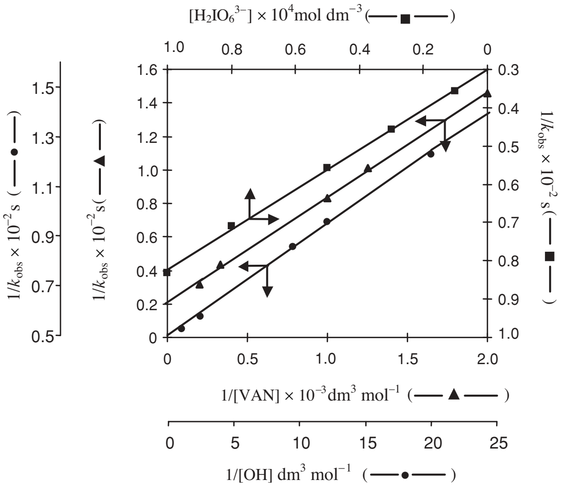


Figure 3 Verification of rate law (8) for the of oxidation of vanillin by diperiodatocuprate(III) at 25°C.

$$\text{rate} = -\frac{\mathrm{d[DPC]}}{\mathrm{d}t} = \frac{2kK_1K_2K_3[\mathrm{DPC}]\,[\mathrm{VAN}]\,[\mathrm{OH^-}]}{[\mathrm{H_2IO_6^{3-}}] + K_1[\mathrm{OH^-}][\mathrm{H_2IO_6^{3-}}] + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3[\mathrm{OH^-}][\mathrm{VAN}]} \tag{7}$$

$$k_{\mathrm{obs}} = \frac{\text{Rate}}{[\mathrm{DPC}]} = \frac{2kK_1K_2K_3\,[\mathrm{VAN}]\,[\mathrm{OH^-}]}{[\mathrm{H_2IO_6^{3-}}] + \mathrm{K_1}[\mathrm{OH^-}]\,[\mathrm{H_2\,IO_6^{3-}}] + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3\,[\mathrm{OH^-}]\,[\mathrm{VAN}]} \tag{8}$$

which explains all the observed kinetic orders of different species.

The rate law (8) can be rearranged into the following form, which is suitable for verification:

$$\frac{1}{k_{\mathrm{obs}}} = \frac{[\mathrm{H_2IO_6^{3-}}]}{2kK_1K_2K_3\,[\mathrm{VAN}]\,[\mathrm{OH^-}]} + \frac{[\mathrm{H_2IO_6^{3-}}]}{2kK_2K_3\,[\mathrm{VAN}]} + \frac{1}{2kK_3\,[\mathrm{VAN}]} + \frac{1}{2k} \tag{9}$$

According to Eq. (9), other conditions being constant, plots of $1/k_{\mathrm{obs}}$ versus $1/[\mathrm{OH^-}]$ ($r \geq 0.995$, $S \leq 0.029$), $1/k_{\mathrm{obs}}$ versus $1/[\mathrm{VAN}]$ ($r \geq 0.997$, $S \leq 0.016$), and $1/k_{\mathrm{obs}}$ versus $[\mathrm{H_2IO_6^{3-}}]$ ($r \geq 0.998$, $S \leq 0.011$)should be linear and are found to be so (Fig. 3). Since pK for the third dissociation of periodate has a magnitude of about 12, at high concentrations of alkali, the concentration of $\mathrm{H_3IO_6^{2-}}$ can be neglected and since periodate in the complex existed prior to the addition of periodate externally, the added periodate can be approximated to $[\mathrm{H_2IO_6^{3-}}]$. The slopes and intercepts of such plots lead to the values of K_1, K_2, K_3, and k as $(4.6 \pm 0.2) \times 10^{-1}$ 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 $(3.7 \pm 0.1) \times 10^{-2}$ s^{-1}, respectively. The equilibrium constant K_1 is far greater than K_2. This may be attributed to the greater tendency of DPC to undergo hydrolysis compared to the dissociation of hydrolyzed species in alkaline medium.

The negligible small 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 can be evaluated as follows. The $[\mathrm{H_2IO_6^{3-}}]$, [VAN], and $[\mathrm{OH^-}]$ (as in Table I) were varied at four different temperatures. The plots of $1/k_{\mathrm{obs}}$ versus $1/[\mathrm{OH^-}]$, $1/k_{\mathrm{obs}}$ versus $1/[\mathrm{VAN}]$, and $1/k_{\mathrm{obs}}$ versus $[\mathrm{H_2IO_6^{3-}}]$ should be linear (Fig. 3). From the slopes and intercepts, the values of K_1 were calculated at different temperatures and these values are given in Table II. A van't Hoff's plot was made for variation of K_1 with temperature (log K_1 vs. $1/T$ ($r \geq 0.9604$, $S \leq 0.006$) 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 II. 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 [32]. 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 II.

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) is more ordered than the reactants [33]. The value of $\Delta S^{\#}$within the range for radical reaction has been ascribed [34] 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. The observed modest enthalpy of activation and a relatively low value of the entropy of activation as well as a higher rate constant of the slow step indicate that the oxidation presumably occurs via inner-sphere mechanism. This conclusion is supported by earlier observation [35].

CONCLUSION

Among various species of DPC in alkaline medium, MPC is considered as active species for the title reaction. The results demonstrate 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, and activation parameters with respect to slow step of reaction were computed. The overall mechanistic sequence described here is consistent with product studies and kinetic studies.

APPENDIX

According to Scheme 1

$$\text{Rate} = \frac{-\mathrm{d}[\mathrm{DPC}]}{\mathrm{d}t} = k[\mathrm{C}] = \frac{2kK_1K_2K_3\,[\mathrm{DPC}][\mathrm{OH}^-][\mathrm{VAN}]}{[\mathrm{H}_2\,\mathrm{IO}_6]^{3-}}$$

$$[\mathrm{DPC}]_\mathrm{T} = [\mathrm{DPC}]_\mathrm{f} + [\mathrm{Cu(H_2IO_6)_2}]^{3-} + [\mathrm{Cu(H_2\,IO_6)(H_2O)_2}] + \mathrm{C} \tag{I}$$

where T and f refer to total and free concentrations

$$= [\mathrm{DPC}]_\mathrm{f}\left\{1 + K_1[\mathrm{OH}^-] + \frac{K_1K_2[\mathrm{OH}^-]}{[\mathrm{H_2IO_6^{3-}}]} + \frac{K_1K_2K_3[\mathrm{OH}^-][\mathrm{VAN}]}{[\mathrm{H_2IO_6^{3-}}]}\right\}$$

$$[\mathrm{DPC}]_\mathrm{f} = \frac{[\mathrm{DPC}]_\mathrm{T}[\mathrm{H_2IO_6^{3-}}]}{[\mathrm{H_2IO_6^{3-}}] + K_1[\mathrm{OH}^-][\mathrm{H_2IO_6^{3-}}] + K_1K_2[\mathrm{OH}^-] + K_1K_2K_3[\mathrm{OH}^-][\mathrm{VAN}]} \tag{II}$$

Similarly, $[\mathrm{OH}^-]_\mathrm{T} = [\mathrm{OH}^-]_\mathrm{f} + [\mathrm{Cu(H_2IO_6)_2}]^{3-} + [\mathrm{Cu(H_2IO_6)(H_2O)_2}]$

$$= [\mathrm{OH}]_\mathrm{f} + K_1[\mathrm{DPC}][\mathrm{OH}^-]_\mathrm{f} + \frac{K_1K_2[\mathrm{DPC}][\mathrm{OH}^-]_\mathrm{f}}{[\mathrm{H_2IO_6^{3-}}]}$$

In view of the low concentration of DPC and $\mathrm{H_2IO_6^{3-}}$ used

$$[\mathrm{OH}]_\mathrm{T} = [\mathrm{OH}]_\mathrm{f}$$

$$[\mathrm{VAN}]_\mathrm{T} = [\mathrm{VAN}]_\mathrm{f} + [\mathrm{C}]$$

$$= [\mathrm{VAN}]_\mathrm{f} + \frac{K_1K_2K_3[\mathrm{DPC}][\mathrm{OH}^-][\mathrm{VAN}]}{[\mathrm{H_2IO_6^{3-}}]} \tag{III}$$

In view of the low concentration of DPC, OH^-, and $\mathrm{H_2\,IO_6^{3-}}$ used,

$$[\mathrm{VAN}]_\mathrm{T} = [\mathrm{VAN}]_\mathrm{f} \tag{IV}$$

Substituting (II), (III), and (IV) in (I) and omitting the subscripts T and f, we get

$$\text{Rate} = \frac{2kK_1K_2K_3[\text{DPC}][\text{VAN}][\text{OH}^-]}{[\text{H}_2\text{IO}_6^{3-}] + K_1[\text{OH}^-][\text{H}_2\text{IO}_6^{3-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{VAN}]}$$

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