

Oxidation of glycine by diperiodatocuprate(III) in aqueous alkaline medium

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Oxidation of the amino acid, glycine, by diperiodatocuprate(III) is studied spectrophotometrically in alkaline medium at constant ionic strength (0.20 mol dm^{-3}) and at varying temperatures (298–318 K). The reaction between diperiodatocuprate(III) and glycine in aqueous alkaline medium exhibits 1:4 stoichiometry. Intervention of free radicals is observed in the reaction. Mechanism involving monoperiodatocuprate(III) as the reactive oxidant species, proceeding through the formation of a complex is proposed. The reaction constants involved in the different steps of the mechanism and activation parameters with respect to the slow step of the mechanism are computed and discussed. The thermodynamic quantities are also determined for the various equilibrium steps. The isokinetic temperature is found to be 381 K.

Keywords: Kinetics, Reaction mechanism, Glycine, Oxidation, Copper

In recent years, the study of the highest oxidation state of transition metals has intrigued many researches. 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)²⁻⁴, and diperiodatonickelate(IV)⁵ are good oxidants in a medium with appropriate pH value. Periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds⁶. The kinetics of self-decomposition of these complexes has been studied in some detail⁷. Copper(III) is shown to be an intermediate in the copper(II)-catalyzed oxidation of amino acids by peroxydisulfate⁸. The oxidation reaction usually involves the copper(II)-copper(I) couple, and such aspects are detailed in different reviews^{9,10}. The use of diperiodatocuprate(III) (DPC) as an oxidant in alkaline medium is new and restricted to a few cases due to its limited solubility and stability in aqueous medium. DPC is a versatile one - electron oxidant for various organic compounds in alkaline medium, and its use as an analytical reagent is now well recognized^{11,12}. Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry^{13,14}. Copper(III) is involved in many biological electro-transfer reactions¹⁵. It has also been used in the differential transition of organic mixtures, in the estimation of chromium, calcium and

magnesium from their ores, and antimony arsenic, and tin from their alloys¹⁶. Since multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is active oxidant.

Glycine ($\text{H}_2\text{NCH}_2\text{COOH}$, GLY) an amino acid is a building block for protein. Glycine is biosynthesized in the human body from the amino acid serine, which is in turn derived from 3-phosphoglycerate. In most organisms, the enzyme serine hydroxymethyltransferase catalyses this transformation via the cofactor pyridoxal phosphate¹⁷.

A literature survey reveals that there are no reports on oxidation of glycine by diperiodatocuprate(III). The present study deals with the title reaction to investigate the redox chemistry of DPC in aqueous alkaline media and to arrive at a suitable mechanism on the basis of kinetic and spectral results and to calculate reaction constants and activation parameters.

Materials and Methods

All chemicals used were of reagent grade and doubly distilled water was used throughout. A solution of glycine was prepared by dissolving an appropriate amount of recrystallised sample in doubly distilled water. The copper(III) periodate complex was prepared by standard procedure^{18,19}. Copper sulphate (3.54 g), potassium periodate (6.80 g), potassium persulphate (2.20 g) and potassium hydroxide (9.0 g) were added to about 250 mL of

water. The order of addition was not important. The mixture was shaken thoroughly and heated on a hot plate. In about 3 hours, the boiling mixture turned intense red and the boiling was continued for 20 minutes more to ensure completion of reaction. The mixture was then cooled, filtered through sintered crucible (G4) and diluted to 250 mL. The persulphate used was just sufficient to oxidize copper(II) to copper(III) and was therefore completely removed during boiling. If an excess of persulphate was used, boiling for a long time is necessary for its complete decomposition. 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 thiocyanate²⁰ method. Periodate solution was prepared by weighing the required amount of sample in hot water and used after 24 hours. Its concentration was ascertained iodometrically²¹ at neutral pH using phosphate buffer. KOH and KNO₃ (BDH) were employed to maintain the required alkalinity and ionic strength, respectively, in the reaction solutions.

Kinetic measurements

The kinetic measurements were made on a Varian Cary 50 Bio UV-visible spectrophotometer. The kinetics was followed under pseudo-first order condition, where [glycine] > [DPC] at 25±0.1 °C, unless specified. The reaction was initiated by mixing the DPC with glycine solution, which also contained the required concentration of KNO₃, KOH and KIO₄ and the progress of the reaction was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC with the molar absorbance index, $\epsilon = 6230 \pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. It was verified that interference from other species present in the reaction mixture at this wavelength was negligible.

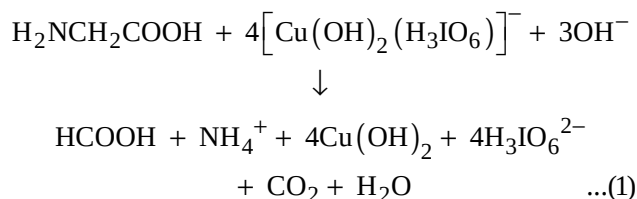
The pseudo-first order rate constants, k_{obs} were determined from the log (absorbance) versus time plots and the rate constants were reproducible within ± 5%. The plots were linear up to 85% completion of reaction in the range of [OH⁻] used. The spectral changes during the reaction show that concentration of DPC decreases with time at 415 nm (Supplementary Data, Fig. S1). During the kinetics, a constant concentration, viz., $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ of KIO₄ was used throughout.

Regression analysis of experimental data was carried out to obtain the regression coefficient r and standard deviation S using Microsoft 2003 Excel program.

Results and Discussion

Stoichiometry and product analysis

Different sets of reaction mixtures containing various ratios of DPC:glycine in the presence of constant amounts of OH⁻ and KNO₃ were kept for 2 hours in closed vessel under nitrogen atmosphere. The unreacted DPC was estimated spectrophotometrically at 415 nm. The results indicate 1:4 stoichiometry as given in Eq. (1).



The main oxidation product was identified as formic acid by a spot test²² and was characterized by NMR spectral studies, {¹H NMR (300 MHz, DMSO); δ 11.2 ppm (s, OH), δ 3.2 ppm (s, C-H)}. Another product, Cu(II), was identified by UV-vis spectra. The byproducts were identified as ammonia by Nessler's reagent while CO₂ was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water.

Reaction order

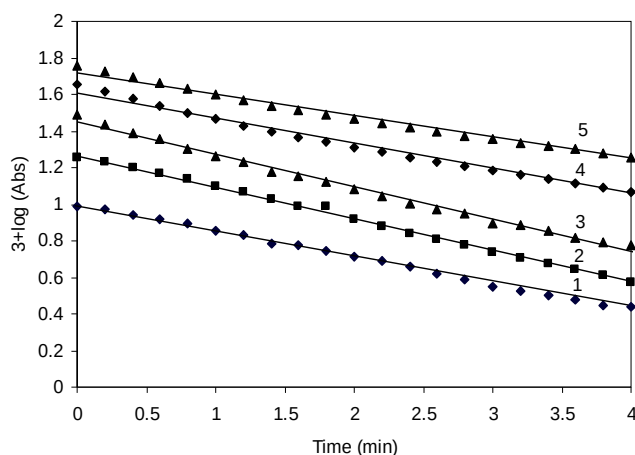
The reaction orders with respect to glycine, alkali and periodate concentrations were determined from the slope of log k_{obs} versus log (concentration) plots by varying the concentrations of reactant, alkali and periodate in turn while keeping all other concentrations and conditions constant.

The concentration of the oxidant (DPC) was varied in the range 1.0×10^{-5} to $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ and the fairly constant k_{obs} values indicate that order with respect to [DPC] was unity (Table 1). This was also confirmed by linearity of log [absorbance] versus time plots ($r \geq 0.991$, $S \leq 0.023$) up to 85% completion of the reaction as shown in Fig. 1.

The effect of glycine on the reaction was studied at constant concentrations of alkali, DPC, and periodate at constant ionic strength of 0.20 mol dm^{-3} . The substrate, glycine, was varied in the range 1.0×10^{-4} to

Table 1—Effect of variation of [DPC], [GLY], [OH⁻] and [IO₄⁻] on the oxidation of glycine by DPC in aqueous alkaline medium at 25 °C. [*I* = 0.20 mol dm⁻³]

[DPC]×10 ⁵ (mol dm ⁻³)	[GLY]×10 ⁴ (mol dm ⁻³)	[OH ⁻] (mol dm ⁻³)	[IO ₄ ⁻]×10 ⁵ (mol dm ⁻³)	<i>k</i> _{obs} ×10 ³ (s ⁻¹)	<i>k</i> _{cal} ×10 ³ (s ⁻¹)
1.0	5.0	0.15	1.0	5.638	5.58
3.0	5.0	0.15	1.0	5.636	5.58
5.0	5.0	0.15	1.0	5.262	5.58
8.0	5.0	0.15	1.0	5.151	5.58
10.0	5.0	0.15	1.0	5.450	5.58
5.0	1.0	0.15	1.0	2.55	2.52
5.0	3.0	0.15	1.0	4.85	5.11
5.0	5.0	0.15	1.0	5.26	5.58
5.0	8.0	0.15	1.0	7.21	7.50
5.0	10.0	0.15	1.0	8.11	8.02
5.0	5.0	0.02	1.0	4.75	4.52
5.0	5.0	0.05	1.0	5.45	5.71
5.0	5.0	0.09	1.0	5.03	6.10
5.0	5.0	0.15	1.0	5.26	5.58
5.0	5.0	0.2	1.0	5.99	6.51
5.0	5.0	0.15	1.0	5.26	5.58
5.0	5.0	0.15	3.0	5.51	5.61
5.0	5.0	0.15	5.0	4.88	5.02
5.0	5.0	0.15	8.0	4.21	4.32
5.0	5.0	0.15	10.0	3.85	4.04

Fig. 1—First order plots for the oxidation of glycine by diperiodatocuprate(III) in aqueous alkaline medium at 298 K. {[DPC]×10⁵ (mol dm⁻³): 1, 1.0; 2, 3.0; 3, 5.0; 4, 8.0; 5, 10.0}.

1.0×10⁻³ mol dm⁻³. The *k*_{obs} values increased with increase in concentration of glycine. The order with respect to [glycine] was found to be less than unity (Table 1) under the experimental conditions (*r* ≥ 0.991, *S* ≥ 0.016).

The effect of increase in concentration of alkali on the reaction was studied at a constant concentrations of glycine, DPC and periodate at a constant ionic strength of 0.20 mol dm⁻³ at 25 °C. The rate constants increased with increase in alkali concentration

(Table 1) and the order with respect to alkali concentration was found to be fractional, i.e., 0.59 (*r* ≥ 0.991, *S* ≤ 0.0155).

The effect of periodate on the reaction was studied in the range of 1.0×10⁻⁵ to 1.0×10⁻⁴ mol dm⁻³, keeping the concentrations of all other reactants constant. It was found that added periodate had a retarding effect on the rate of reaction (Table 1), the order with respect to periodate concentration being negative and less than unity, i.e., -0.39 (*r* ≥ 0.899, *S* ≤ 0.0211).

The effect of ionic strength was studied by varying the potassium nitrate concentration. Ionic strength was varied from 0.30 mol dm⁻³ to 0.60 mol dm⁻³ at constant concentrations of DPC, glycine, periodate and alkali. The *k*_{obs} values increased with increase in ionic strength. The plot of log *k*_{obs} versus *I*^{1/2} was linear with positive slope (0.56) (Supplementary Data, Fig. S2). The dielectric constant of the medium, *D*, was varied by varying the *t*-butyl alcohol–water percentage. The dielectric constants of the reaction medium at various composition of *t*-butyl alcohol–water (v/v) were calculated from the equation, *D* = *V*₁*D*₁ + *V*₂*D*₂, where *D*₁ and *D*₂ are dielectric constants of pure water and *t*-butyl alcohol, i.e., 78.5 and 10.9 at 25 °C respectively, and, *V*₁ and *V*₂ are the volume fractions of the components water and *t*-butyl alcohol respectively, in the total volume

of mixture. The dielectric constant of the medium had no effect on the rate of the reaction.

The externally added product, copper(II) (CuSO_4) and formic acid did not have any significant effect on the rate of the reaction.

Under the experimental conditions, the rate law is given as

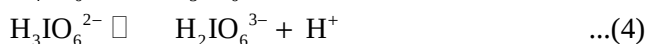
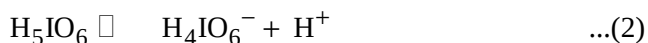
$$\text{Rate} = k_{\text{obs}} [\text{GLY}]^{0.59} [\text{DPC}]^{1.00} [\text{OH}^-]^{0.59} [\text{IO}_4^-]^{-0.39}$$

The kinetics was studied at four different temperatures, i.e., 30, 35, 40 and 45 °C for standard conditions. The rate constants were found to increase with increase in temperature. The energy of activation corresponding to these constants was evaluated from the linear Arrhenius plot of $\log k_{\text{obs}}$ versus $1/T$ (Supplementary Data, Fig. S3; $r = 0.982$, $S \leq 0.0159$) and along with other activation parameters obtained are tabulated in Table 2.

To examine the intervention of free radicals in the reaction, the reaction mixture, to which a known quantity of acrylonitrile monomer was initially added, was kept for 2 hours in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radical in the reaction. The blank experiments with either DPC or glycine alone with acrylonitrile did not induce any polymerization under the same conditions as those for reaction mixture. Initially, the added acrylonitrile decreases the rate of reaction, indicating free-radical intervention, which is the case as reported in literature^{23, 24}.

Reaction mechanism

The water soluble copper(III) periodate complex is reported²⁵ to be $[\text{Cu}(\text{HIO}_6)_2]^{5-}$. However, in aqueous alkaline medium and at the 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 equilibria²⁶ depending on the pH of the solution, as discussed below.



Periodic acid exists in the acid medium as H_5IO_6 and as H_4IO_6^- at 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

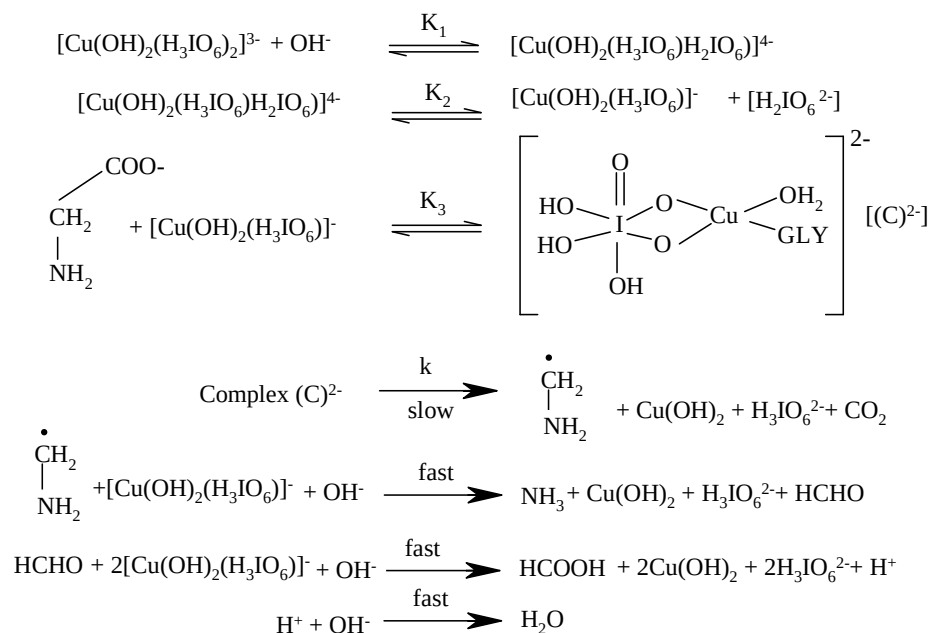
Table 2—Effect of temperature on the mechanism and activation parameters for the oxidation of glycine by alkaline diperiodatocuprate(III). {[DPC] = 5×10^{-5} mol dm⁻³; [GLY] = 4×10^{-4} mol dm⁻³; [OH⁻] = 0.15 mol dm⁻³; [IO₄⁻] = 1×10^{-5} mol dm⁻³}

<i>T</i> (K)	<i>k</i> _{obs} × 10 ³ (s ⁻¹)
298	5.26
303	8.86
308	13.45
313	16.19
318	26.92
<i>E</i> _a (kJ mol ⁻¹)	60.3
Δ <i>H</i> [#] (kJ mol ⁻¹)	59.7
Δ <i>S</i> [#] (J K ⁻¹ mol ⁻¹)	-94.7
Δ <i>G</i> [#] (kJ mol ⁻¹)	87.9
log <i>A</i>	11.3

dimerise²⁷. 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), $[\text{Cu}(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{2-}$, a conclusion also supported by earlier work²⁸.

Lister²⁹ proposed three forms of copper(III) periodate in alkaline medium, viz., diperiodatocuprate(III) (DPC), monoperiodatocuprate(III) (MPC), and tetrahydroxocuprate(III). The last one is ruled out, as its equilibrium constant is 8.0×10^{-11} at 40 °C. Hence, in the present study, DPC and MPC are considered as the 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 DPC. The results of increase in the rate with increase in alkaline concentration and decrease in rate with increase in periodate concentration suggest that equilibria of different copper(III) periodate complexes are possible.

The reaction between the diperiodatocuprate(III) complex and glycine in alkaline medium has a 1:4 stoichiometry (GLY:DPC) with a first order dependence on [DPC], less than unit order in [substrate] and [alkali] and a negative fractional order in [periodate]. No effect of the added products was observed. Based on the experimental results, a mechanism is proposed in which all the observed orders in each constituent such as [oxidant], [reductant], [OH⁻], and [IO₄⁻] are well accommodated. It is known that glycine exists in the form of a zwitterion³⁰ in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium it is in the fully deprotonated form³⁰. The increase in reaction rate with increase in



Scheme 1

alkalinity (Table 1) and also decrease in rate with increase in $[\text{H}_3\text{IO}_6^{2-}]$ (Table 1) suggest an equilibrium of the copper(III) periodate complex to form a monoperiodatocuprate(III) (MPC) species. Similar results have been well reported in literature³¹. It is expected that a lower periodate complex such as monoperiodatocuprate(III) plays an important role in the reaction. The inverse fractional order in $[\text{H}_3\text{IO}_6^{2-}]$ may also be due to MPC. Therefore, MPC may be the main reactive form of the oxidant.

The less than unit order in [glycine] is due to the formation of a complex (C) between the oxidant and glycine prior to the formation of the products. K_3 is the composite equilibrium constant comprising the equilibrium to bind active species of glycine to MPC species to form a complex (C). Then, this complex (C) decomposes in a slow step to form a free radical derived from glycine. This free-radical species further reacts with another molecule of MPC species in a fast step to yield ammonia and formaldehyde. The formaldehyde obtained further reacts with two molecules of MPC to form formic acid. The detailed mechanism for the oxidation of glycine by diperiodatocuprate(III) is represented as given in Scheme 1.

Since Scheme 1 is in accordance with 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

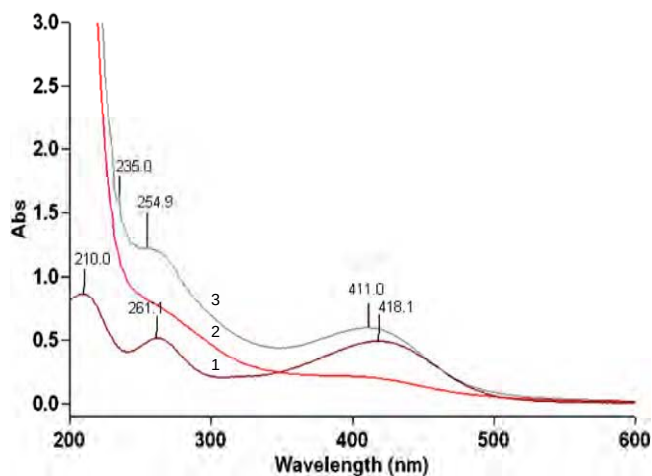


Fig. 2—UV-vis spectral evidence for the complex formation between DPC and glycine. [1, DPC (261.1 nm); 2, glycine; 3, glycine + DPC (254.9 nm)].

scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work^{32,33}. Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-vis spectra of glycine ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$), DPC ($5.0 \times 10^{-5} \text{ mol dm}^{-3}$), $[\text{OH}^-] = 0.15 \text{ mol dm}^{-3}$ and a mixture of both. A hypsochromic shift of 6.2 nm from 261.1 to 254.9 nm was observed in the spectra of DPC as shown in Fig. 2. The Michaelis-Menten plot also proved the complex formation between DPC and glycine, which

explains the less than unit order dependence on [glycine]. Such a complex between a substrate and an oxidant has been observed in the other studies³⁴.

According to Scheme 1, the rate law is given as Eq. (5), (For derivation see Supplementary Data, Rate derivation).

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{DPC}]} = \frac{kK_1K_2K_3[\text{GLY}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{GLY}]} \quad \dots(5)$$

By rearranging the above Eq. (5) we get Eq. (6) which is suitable for verification.

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_1K_2K_3[\text{OH}^-][\text{GLY}]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_2K_3[\text{GLY}]} + \frac{1}{K_2K_3[\text{GLY}]} + \frac{1}{k} \quad \dots(6)$$

According to Eq. (6), other conditions being constant, plots of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ ($r \geq 0.9891$, $S \leq 0.0133$), $1/k_{\text{obs}}$ versus $1/[\text{GLY}]$ ($r \geq 0.9982$, $S \leq 0.0122$), $1/k_{\text{obs}}$ versus $[\text{H}_3\text{IO}_6^{2-}]$ ($r \geq 0.9922$, $S \leq 0.0144$) are linear (Fig. 3). The slopes and intercepts of such a plots lead to the values of k , K_1 , K_2 and K_3 as $0.907 \pm 0.04 \times 10^{-2} \text{ s}^{-1}$, $81.98 \pm 4.0 \text{ dm}^3 \text{ mol}^{-1}$, $7.56 \pm 0.3 \times 10^{-5} \text{ mol dm}^{-3}$, $3.79 \pm 0.18 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ respectively. Using these K_1 , K_2 , K_3 , and k values, the rate constants under different experimental conditions were calculated by Eq. (5) and compared with experimental data (Table 1). There is a good agreement between the two values which supports the proposed mechanism in Scheme 1. The equilibrium constant K_1 is far greater than K_2 which may be attributed to the greater tendency of DPC to undergo hydrolysis as compared to the dissociation of hydrolyzed species in alkaline medium. The increase in k_{obs} with increase in ionic strength explains qualitatively the involvement of an anionic molecule in the reaction. All these results are interpreted satisfactorily in Scheme 1.

The values of $\Delta H^\ddagger$ (59.7 kJ mol^{-1}) and $\Delta S^\ddagger$ ($-94.7 \text{ J K}^{-1} \text{ mol}^{-1}$) are both favorable for an electron transfer process. The negative value of $\Delta S^\ddagger$ ($-94.7 \text{ J K}^{-1} \text{ mol}^{-1}$) indicates that the complex (C) is more ordered than the reactants³⁵. The values of $\Delta S^\ddagger$ within the range for the radical reaction may be ascribed to the nature of electron pairing and unpairing processes and to the loss of degree of

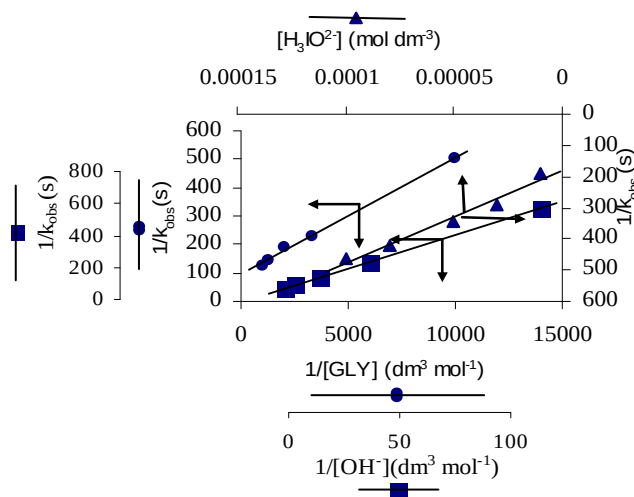


Fig. 3—Verification of rate law (5) in the form of (6) for the oxidation of glycine by diperiodatocuprate(III). {1, Plot of $1/k_{\text{obs}}$ versus $1/[\text{GLY}]$; 2, Plot of $1/k_{\text{obs}}$ versus $[\text{H}_3\text{IO}_6^{2-}]$; 3, Plot of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ }.

freedom earlier available to the reactants upon the formation of rigid transition state³⁶. The observed enthalpy of activation and a relatively low value of the entropy of activation as well as a higher rate constant of the slow step of Scheme 1 indicate that the oxidation is likely to occur via an inner sphere mechanism. This conclusion is also supported by earlier observations³⁷.

Conclusions

Among various species of DPC in alkaline medium, monoperiodatocuprate(III) $[\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)]^-$ is considered as the active species for the title reaction. The results indicated that the role of pH in the reaction medium is crucial. The rate constant of the slow step and other equilibrium constants involved in the mechanism as well as the activation parameters of the reaction have been computed. The overall mechanistic sequence described herein is consistent with product studies and kinetic studies.

Supplementary data

Supplementary data associated with this article, i.e., Figs S1-S3 and Rate derivation, are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_52A\(02\)200-206_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_52A(02)200-206_SupplData.pdf).

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