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A Kinetic and Mechanistic Study on the Oxidation of L-Cystine by Alkaline Diperiodatocuprate(III): A Free Radical Intervention[1]

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Abstact—The kinetics of oxidation of L-cystine (L-CYS) by diperiodatocuprate (III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.20 mol/1 was studied spectrophotometrically at 298 K. The reaction between DPC and L-cystine in alkaline medium exhibits 1 : 4 stoichiometry (L-cystine: DPC =1 : 4). The reaction is of first order in [DPC] and has less than unit order in [L-CYS] and [alkali], negative fractional order in [periodate] and intervention of free radicals was observed in the reaction. The oxidation reaction in alkaline medium has been shown to proceed via a monoperiodatocuprate(III)-L-ystine 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 GC-MS. 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 were also determined.

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Amino acids act not only as the building blocks in protein synthesis but they also play a significant role in metabolism and have been oxidized by different oxidizing agents. The study of the oxidation of amino acids is of interest because of their biological significance and selectivity towards the oxidant to yield the different products [1–3].

L-cystine is a covalently linked dimeric non-essential amino acid formed by the oxidation of cystine. Two molecules of L-cysteine are joined together by a disulfide bridge (S–S) to form L-cystine. L-cystine is sulfur containing chemical substance, which naturally occurs as a deposit in the urine, and can form a calculus (hard mineral formation) when deposited in the kidney. L-cystine is required for proper vitamin B6 utilization and is also helpful in the healing of burns and wounds breaking down mucus deposits in illnesses such as bronchitis as well as cystic fibrosis. L-cystine also assists in the supply of insulin to the pancreas.

In recent years, the study of 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) [4], diperiodatoargentate(III) [5] and diperiodatonickelate(IV) [6] are good oxidants in a medium with an appropriate pH value. Periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds [7]. The kinetics of self-decomposition of these complexes was studied in some detail [8]. Copper(III) is shown to be an intermediate in the copper(II) catalyzed oxidation of amino acids by peroxydisulphate [9]. The oxidation reaction usually involves the copper (II)-copper(I) couple and such aspects are detailed in different reviews [10, 11]. The use of diperiodatocuprate(III) (DPC) as an oxidant in alkaline medium is new and restricted to a few cases due to the fact of 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 [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 electron transfer reactions [15]. They have also been used [16] in the differential titration of organic mixtures, in the estimation of chromium, calcium and magnesium from their ores, antimony, arsenic and tin from their alloys. Since multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is the active oxidant.

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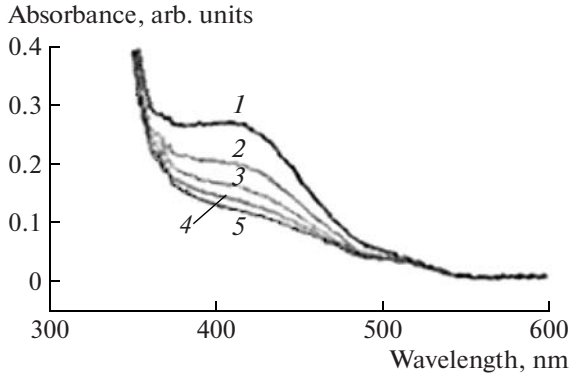


Fig. 1. Spectroscopic changes occurring in the oxidation of L-cystine by diperiodatocuprate(III) at 25°C ([DPC] = 5.0×10^{-5}, [L-CYS] = 5.0×10^{-4}, [OH^-] = 0.08, [I] = 0.20 mol/l. Scanning time interval 0.5 min (curves *1*–*5*).

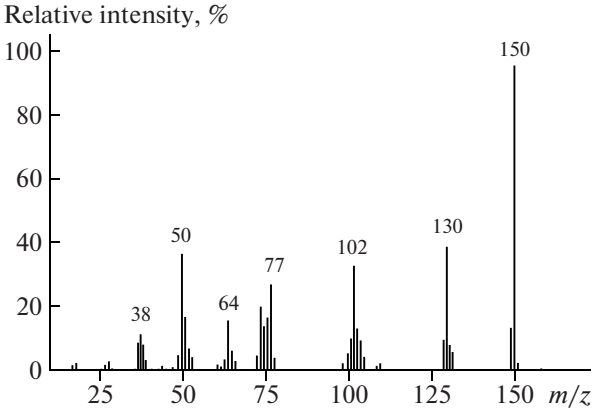


Fig. 2. GC-mass spectrum of acetaldehyde (2-oxo-ethyldisulfanyl) with its molecular ion peak at 150 amu.

Literature survey reveals that there are no reports on the oxidation of L-cystine (L-CYS) by diperiodatocuprate(III). The present study deals with the title reaction to investigate the redox chemistry of DPC in alkaline media to arrive at a suitable mechanism on the basis of kinetic and spectral results and to compute the thermodynamic quantities of various steps of Scheme.

EXPERIMENTAL

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of L-cystine (BDH Industries Ltd.) was prepared by dissolving an appropriate amount of recrystallised sample in double distilled water. The purity of L-cystine sample was checked its m.p. 239°C (literary m.p. 240°C). The required concentration of L-cystine was used from its stock solution. The copper(III) periodate complex was prepared by standard procedure [17]. 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 thiocyanate method [18]. The copper(II) solutions were prepared by dissolving the known amount of copper sulphate (BDH) in distilled water. Periodate solution was prepared by weighing out the required amount of sample in hot water and used after keeping it for 24 h to maintain the equilibrium. Its concentration was ascertained iodometrically [19] at neutral pH by phosphate buffer. Since periodate is present in excess in DPC, the possibility of oxidation of L-cystine by periodate in alkaline medium at 25°C was tested. The progress of the reaction was followed iodometrically. It was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of L-cystine. KOH and KNO_3 (BDH, AR) were employed to maintain the required alkalinity and ionic strength respectively in reaction solutions.

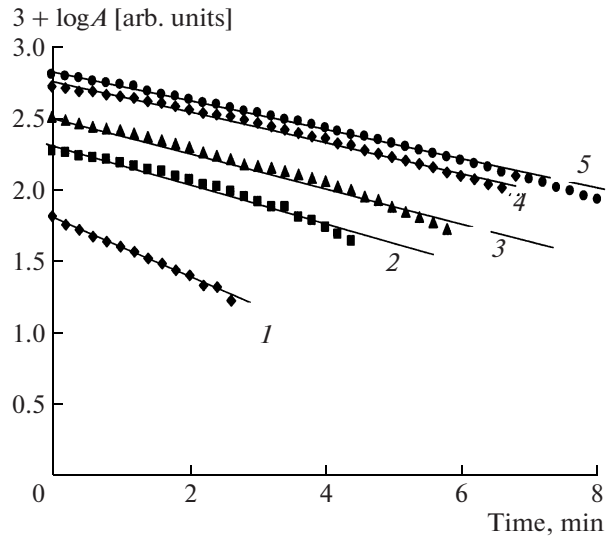


Fig. 3. First order plots for the oxidation of L-cystine by diperiodatocuprate(III) in aqueous alkaline medium at 25°C. [Diperiodatocuprate(III)] × 10^5, mol/l: (*1*) 1.0, (*2*) 3.0, (*3*) 5.0, (*4*) 8.0, (*5*) 10.0.

The kinetic measurements were performed on a Varian CARY 50 Bio UV-Visible Spectrophotometer. The kinetics was followed under pseudo-first order condition where [L-CYS] > [DPC] at 25 ± 0.1°C, unless specified. The reaction was initiated by mixing the DPC to L-cystine solution which also contained required concentration of KNO_3, KOH, and KIO_4; and the progress of reaction was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC with the molar absorbancy index $\varepsilon = 6230 \pm 100$ l 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. During the kinetics a constant concentration viz. 1.0×10^{-4} mol/l of KIO_4 was used throughout the study unless otherwise stated.

Kinetics runs were also 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.

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 Excel-2003 programme.

RESULTS AND DISCUSSION

Stoichiometry and Product Analysis

Different sets of reaction mixtures containing varying ratios of DPC to L-cystine in presence constant amounts of OH^- and KNO_3 were kept for 6 h in closed vessel under inert atmosphere. The remaining DPC concentration was estimated by spectrophotometrically at 415 nm. The results indicate 1 : 4 (L-CYS : DPC) stoichiometry as given in Eq. (I).

$$\begin{aligned} &\mathrm{HOOC{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CH_2{-}S{-}S{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}COOH + 4[Cu(OH)_2(H_3IO_6)]^-} \\ &\xrightarrow{2H_2O} \mathrm{OHC{-}CH_2{-}S{-}S{-}CH_2{-}CHO + 2NH_3 + 4Cu(OH)_2 + 4H_3IO_6^{2-} + 2CO_2 + 4H^+} \end{aligned} \qquad \text{(I)}$$

The main reaction product was identified as (2 oxo-ethyl disulfanyl)-acetaldehyde by its IR spectrum (KBr): carbonyl stretching at 1742 cm^{-1} and a band at 2854 cm^{-1} due to aldehydic –CH stretching. Nessler's reagent identified ammonia. Preparing its 2,4-DNP derivative identified the product aldehyde.

Table 1. Effect of [DPC], [L-CYS], [OH^-], and [IO_4^-] on the oxidation of L-cystine by diperiodatocuprate(III) in alkaline medium at 25°C ($I = 0.20$ mol/l)

[DPC] × 10^5, mol/l	[L-CYS] × 10^4, mol/l	[OH^-], mol/l	[IO_4^-] × 10^4, mol/l	$k_{obs} \times 10^3$, s^{-1}	$k_{cal} \times 10^3$, s^{-1}
1.0	5.0	0.08	1.0	6.1	6.2
3.0	5.0	0.08	1.0	6.0	6.2
5.0	5.0	0.08	1.0	6.1	6.2
8.0	5.0	0.08	1.0	5.9	6.2
10.0	5.0	0.08	1.0	6.0	6.2
5.0	3.0	0.08	1.0	4.3	4.2
5.0	5.0	0.08	1.0	6.1	6.3
5.0	10.0	0.08	1.0	10.0	10.0
5.0	20.0	0.08	1.0	14.9	14.3
5.0	30.0	0.08	1.0	17.5	16.7
5.0	5.0	0.02	1.0	4.7	4.6
5.0	5.0	0.05	1.0	5.5	5.8
5.0	5.0	0.08	1.0	6.1	6.3
5.0	5.0	0.10	1.0	6.5	6.4
5.0	5.0	0.20	1.0	7.0	6.7
5.0	5.0	0.08	0.5	7.0	6.7
5.0	5.0	0.08	0.8	6.4	6.4
5.0	5.0	0.08	1.0	6.1	6.3
5.0	5.0	0.08	3.0	5.1	4.9
5.0	5.0	0.08	5.0	4.2	4.1

Additionally GC-MS analysis was carried out on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer.

The mass spectra confirmed the presence of (2-oxo-ethyldisulfanyl)-acetaldehyde (Fig. 2), which showed both molecular ion peak and base peak at $m/z = 150$. All other peaks observed in GC-MS can be interpreted in accordance with the observed structure of the (2-oxo-ethyldisulfanyl)-acetaldehyde.

Reaction Orders

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

The oxidant DPC concentration was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol/l and the fairly constant k_{obs} values indicate that order with respect to [DPC] was one (Table 1). This was also confirmed by linearity of the plots of log$A$ versus time ($r \geq 0.983$, $S \leq 0.012$) up to 80% completion of the reaction (Fig. 3). The effect of L-cystine on the rate of reaction was studied at constant concentrations of alkali, DPC and periodate at a constant ionic strength of 0.20 mol/l. The substrate L-cystine was varied in the range of 3.0×10^{-4} to 3.0×10^{-3} mol/l. The k_{obs} values increased with increase in concentration of L-cystine. The order with respect to [L-cystine] was found to be less than unity (Table 1) ($r \geq 0.998$, $S \leq 0.008$). The effect of alkali on the reaction has been studied in the range of 0.02 to 0.20 mol/l at constant concentrations of L-cystine, DPC and a constant ionic strength of 0.20 mol/l. The rate constants increased with increasing [alkali] and the order was found to be less than unity ($r \geq 0.981$, $S \leq 0.006$) (Table 1). The effect of increasing concentration of periodate was studied by varying

the periodate concentration from 5.0×10^{-5} to 5.0×10^{-4} mol/l 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 1).

It was found that ionic strength and dielectric constant of the medium had no significant effect on the rate of reaction. The externally added products, (2-oxo-ethyldisulfanyl)-acetaldehyde and copper(II) ($CuSO_4$), did not have any significant effect on the rate of the reaction.

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 of polymer was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either DPC or L-cystine alone with acrylonitrile did not induce any polymerization under the same condition as those induced for reaction mixture. Initially added acrylonitrile decreased the rate of reaction indicating free radical intervention, which is the case in earlier work [20].

The kinetics was studied at four different temperatures under varying concentrations of L-cystine, alkali and periodate, keeping other conditions constant. The rate constants were found to increase with increase in temperature. The rate constant (k) of the slow step of Scheme were obtained from the slopes and intercepts of $1/k_{obs}$ versus 1/[L-CYS], $1/[OH^-]$, and $[H_3IO_6^{2-}]$ 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 $1/T$ ($r \geq 0.9802$, $S \leq 0.009$) and other activation parameters obtained are tabulated in Table 2.

The water-soluble copper(III) periodate complex is reported [21] to be $[Cu(HIO_6)_2(OH)_2]^{7-}$. However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as HIO_6^{4-} (as present in the complex) as is evident from its involvement in the multiple equilibria [22] (II)–(IV) depending on the pH of the solution.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+, \quad \text{(II)}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+, \quad \text{(III)}$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+. \quad \text{(IV)}$$

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 dimerise [23]. 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), $[Cu(H_3IO_6)_2(OH)_2]^{3-}$, a conclusion also supported by earlier work [24].

The reaction between the diperiodatocuprate(III) complex and L-cystine in alkaline medium had a stoichiometry 1 : 4 (L-CYS : DPC) with a first order dependence on [DPC], apparent less then unite order in [L-CYS] and [OH] and a negative fractional order in [periodate]. No effect of added products was observed.

The result of increase in rate of reaction with increase in alkalinity (Table 1) can be explained in terms of prevailing equilibrium of formation of $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$ from $[Cu(OH)_2(H_3IO_6)_2]^{3-}$ deprotonated DPC as given in the following Eq. (V).

$$[Cu(OH)_2(H_3IO_6)_2]^{3-} + OH^- \xrightleftharpoons{K_1} [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + H_2O. \quad \text{(V)}$$

Also decrease in rate with increase in $[H_3IO_6^{2-}]$ (Table I) suggest that equilibrium of copper(III) periodate complex to form monoperiodatocuptrate(III) (MPC) species as given in Eq. (VI) is established.

$$[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} \xrightleftharpoons{K_2} [Cu(OH)_2(H_3IO_6)]^- + [H_2IO_6]^{3-}. \quad \text{(VI)}$$

Such type of equilibria (V) and (VI) have been well noticed in literature [25]. It may be expected that a lower periodate complex such as 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 [L-CYS] presumably results from formation of a complex (C) between the MPC species and L-cystine prior to the formation of the products. This complex C decomposes in a slow step to form a free radical derived from L-cystine. This free radical species further reacts with another molecule of MPC in a fast step to form 2-amino-3-propionic acid intermediate, This intermediate then reacts with two more molecules of MPC in a further fast steps to form the products as given in Scheme.

$$[Cu(OH)_2(H_3IO_6)_2]^{3-} + OH^- \overset{K_1}{\rightleftharpoons} [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + H_2O$$

$$[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} \overset{K_2}{\rightleftharpoons} [Cu(OH)_2(H_3IO_6)]^- + H_2IO_6^{3-}$$

$$[Cu(OH)_2(H_3IO_6)]^- + HOOC{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CH_2{-}S{-}S{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}COOH \overset{K_3}{\rightleftharpoons} \text{Complex(C)}$$

$$\text{Complex(C)} \overset{\underset{k}{\text{Slov}}}{\rightleftharpoons} HOOC{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CH_2{-}S{-}S{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{\dot{C}H}} + Cu(OH)_2 + H_3IO_6^{2-} + H^+ + CO_2$$

$$HOOC{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CH_2{-}S{-}S{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{\dot{C}H}} + [Cu(OH)_2(H_3IO_6)]^-$$

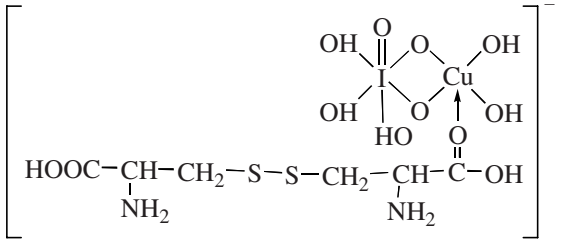
$$\xrightarrow[H_2O]{\text{fast}} HOOC{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CH_2{-}S{-}S{-}CH_2{-}CHO + NH_3 + H^+ + Cu(OH)_2 + H_3IO_6^{2-}$$

$$HOOC{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CH_2{-}S{-}S{-}CH_2{-}CHO + [Cu(OH)_2(H_3IO_6)]^- \xrightarrow{\text{fast}} \underset{\displaystyle NH_2}{\underset{|}{\dot{C}H}}{-}CH_2{-}S{-}S{-}CH_2{-}CHO$$
$$+ Cu(OH)_2 + H_3IO_6^{2-} + CO_2 + H^+$$

$$\underset{\displaystyle NH_2}{\underset{|}{\dot{C}H}}{-}CH_2{-}S{-}S{-}CH_2{-}CHO + [Cu(OH)_2(H_3IO_6)]^- \xrightarrow[H_2O]{\text{fast}} OHC{-}CH_2{-}S{-}S{-}CH_2{-}CHO$$
$$+ NH_3 + Cu(OH)_2 + H_3IO_6^{2-} + H^+$$

Scheme.

Since Scheme is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility (see IR spectra). This type of radical intermediate has also been observed in earlier work [26]. The probable structure of the complex is given by:



Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-Vis spectra of L-cystine (5.0×10^{-4} mol/l), DPC (5.0×0^{-5} mol/l), $[OH^-] = 10.08$ (mol/l) and mixture of both. A bathochromic shift of about 4 nm from 365 to 369 nm in the spectra of L-cystine was observed. The Michael is-Menten plot also proved the complex formation between DPC and L-cystine, which explains the less than unit order dependence on [L-CYS]. Such type of complex between a substrate and an oxidant has been observed in other studies [26].

Scheme leads to the rate law (1):

$$\text{Rate} = \frac{-d[DPC]}{dt} = \frac{kK_1K_2K_3[\text{L-CYS}][OH^-][Cu(OH)_2(H_3IO_6)_2]^{3-}}{[H_2IO_6^{3-}]}, \quad (1)$$

$$\frac{\text{Rate}}{[DPC]} = k_{obs} = \frac{kK_1K_2K_3[\text{L-CYS}][OH^-]}{[H_2IO_6^{3-}] + K_1K_2K_3[OH^-][\text{L-CYS}] + K_1K_2[OH^-] + K_1[H_2IO_6^{3-}][OH^-]}. \quad (2)$$

Table 2. Thermodynamic activation parameters for the oxidation of L-cystine by DPC in aqueous alkaline medium with respect to the slow step of Scheme

A. Effect of temperature

Temperature, K	$k \times 10^2$, s^{-1}
293	1.66
298	2.50
303	5.64
308	8.14

B. Activation parameters (Scheme)

Parameters	Values
E_a	83 ± 1 kJ/mol
$\Delta H^{\#}$	81 ± 2 kJ/mol
$\Delta G^{\#}$	82 ± 3 kJ/mol
log$A$	13.0 ± 0.2

C. Effect of temperature to calculate K_1, K_2, and K_3 for the oxidation of L-cystine by diperiodatocuprate(III) in alkaline medium

Temperature, K	K_1, mol/l	$K_2 \times 10^2$, mol/l	$K_3 \times 10^{-2}$, l/mol
293	0.12 ± 0.01	0.76 ± 0.03	8.5 ± 0.2
298	1.27 ± 0.04	0.50 ± 0.02	8.1 ± 0.1
303	1.98 ± 0.04	0.24 ± 0.05	6.6 ± 0.3
308	3.38 ± 0.05	0.17 ± 0.05	5.7 ± 0.3

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, kJ/mol	154 ± 3	−77.4 ± 0.8	−20.5 ± 0.8
ΔS, J K^{-1} mol^{-1}	520 ± 10	−303 ± 5	−13.1 ± 0.8
ΔG_{298}, kJ/mol	−0.6 ± 0.3	13.1 ± 0.8	−16.6 ± 0.8

Table 3. The rate constant of the slow steps at different temperatures of some acids (for isokinetic temperature)

Amino acids	k_1 at 298 K, l mol^{-1} s^{-1}	k_2 at 303 K, l mol^{-1} s^{-1}	Reference
L-Tryptophan	0.014	0.019	[30]
L-Aspartic acid	0.012	0.016	[31]
L-Lysine	0.021	0.041	[32]
L-Cystine	0.025	0.056	Present work

This explains all the observed kinetic orders of different species. The rate law (2) can be rearranged in to the following form, which is suitable for verification:

$$\frac{1}{k_{obs}} = \frac{[H_2IO_6^{3-}]}{kK_1K_2K_3[OH^-][\text{L-CYS}]} + \frac{[H_2IO_6^{3-}]}{kK_2K_3[\text{L-CYS}]} + \frac{1}{kK_3[\text{L-CYS}]} + \frac{1}{k}. \quad (3)$$

According to equation (3), other conditions being constant, plots of $1/k_{obs}$ versus 1/[OH] ($r \geq 0.996$, $S \leq 0.014$), $1/k_{obs}$ versus 1/[L-CYS] ($r \geq 0.992$, $S \leq 0.012$) and $1/k_{obs}$ versus $[H_3IO_6^{2-}]$ ($r \geq 0.987$, $S \leq 0.011$) should be linear and are found to be so (Fig. 4). The slopes and intercepts of such plots lead to the values of K_1, K_2, K_3 and k as (1.27 ± 0.04) mol/l, (0.50 ± 0.02) × 10^{-2} mol/l, (8.15 ± 0.12) × 10^2 1/mol, and (2.50 ± 0.01) ± 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 value of k_1 is good agreement with earlier literature [25].

The thermodynamic quantities for the first, second and third equilibrium steps of Scheme can be evaluated as follows. The $[H_3IO_6^{2-}]$, [L-CYS], 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/[L-CYS] and $1/k_{obs}$ versus $[H_3IO_6^{2-}]$ should be linear (Fig. 4). From the slopes and intercepts, the values of K_1, K_2, and K_3 were calculated at different temperatures and these values are given in Table 2. The vant Hoff's plots were made for variation of K_1, K_2, and K_3 with temperature (logK_1 versus $1/T$ ($r \geq 0.985$, S ≤ 0.004), logK_2 versus $1/T$ ($r \geq 0.973$, $S \leq 0.007$), and log K_3 versus $1/T$ ($r \geq 0.992$, $S \leq 0.008$)) and the values of enthalpy of reaction ΔH and free energy of reaction ΔG were calculated for the first, second and third equilibrium steps. These values are given in Table 2. A comparison of the thermodynamic quantities of first step of Scheme 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 [27].

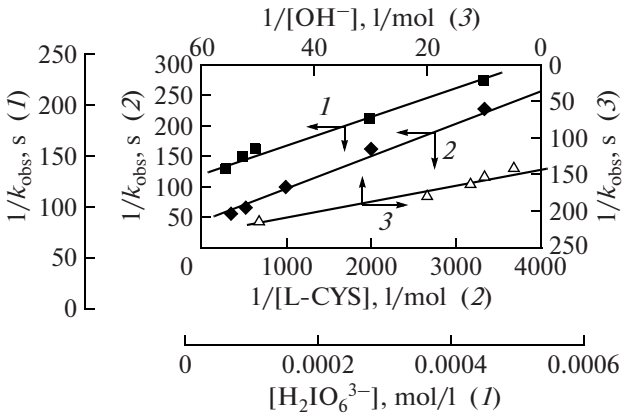


Fig. 4. Verification of rate law (1) for the of oxidation of L-cystine by diperiodatocuprate(III) at 25°C.

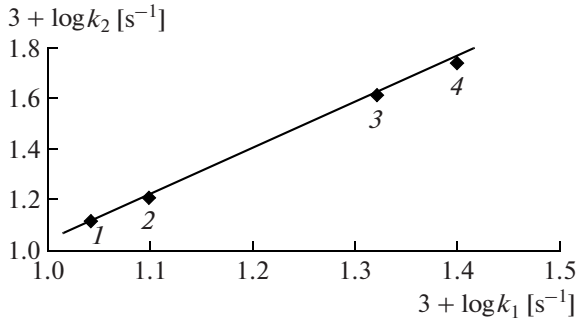


Fig. 5. Plot of $\log k_2$ at 303 K versus $\log k_1$ at 298 K for isokinetic temperature (Table 3): (*1*) L-tryptophan, (*2*) L-aspartic acid, (*3*) L-lysine, (*4*) L-cystine.

The rate constants of the slow step at different temperature of some acids by DPC are summarized in Table 3. According to Exner [28], if the rates of several reactions in a series have been measured at two temperatures and $\log k_2$ (at T_2) is linearly related to $\log k_1$ (at T_1), i.e., $\log k_2 = a + b \log k_1$, he proposes that β can be evaluated from the equation

$$\beta = T_1 T_2 (b - 1)/T_2 b - T_1. \qquad \text{(V)}$$

We have calculated the isokinetic temperature to be 287 K by plotting $\log k_2$ at 303 K versus $\log k_1$ at 298 K (Fig. 5). The value of β (287 K) is lower than experimental temperature (298 K). This indicates that the rate is governed by the enthalpy of activation [29]. The linearity and the slope of the plot obtained may confirm that the kinetics of this reaction follows a similar mechanism, as previously suggested.

Among various species of DPC in alkaline medium, monoperiodatocuprate(III) is considered as active species for the title reaction. The results indicate that 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, mechanistic and kinetic studies.

APPENDIX

According to Scheme,

$$\text{Rate} = \frac{-\mathrm{d}[\text{DPC}]}{\mathrm{d}t} = k[\text{C}] = \frac{kK_1K_2K_3[\text{L-CYS}][\text{OH}^-][\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)_2]^{3-}}{[\text{H}_2\text{IO}_6^{3-}]}, \qquad \text{(A.1)}$$

$$\begin{aligned}[\text{DPC}]_t &= [\text{DPC}]_f + [\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{4-} + [\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)]^- + [\text{C}] \\ &= [\text{DPC}]_f\left[\frac{[\text{H}_2\text{IO}_6^{3-}] + K_1[\text{H}_2\text{IO}_6^{3-}][\text{OH}^-] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-CYS}]}{[\text{H}_2\text{IO}_6^{3-}]}\right],\end{aligned} \qquad \text{(A.2)}$$

where $[\text{DPC}]_t$ and $[\text{DPC}]_f$ refer to total and free DPC concentrations respectively. The free [DPC] is given by

$$[\text{DPC}]_f = \frac{[\text{DPC}]_t[\text{H}_2\text{IO}_6^{3-}]}{[\text{H}_2\text{IO}_6^{3-}] + K_1[\text{H}_2\text{IO}_6^{3-}][\text{OH}^-] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-CYS}]}. \qquad \text{(A.3)}$$

Similarly total $[\text{OH}^-]$ can be calculated as

$$[OH^-]_t = [OH^-]_f + [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + [Cu(OH)_2(H_3IO_6)]^- + [C] \quad (A.4)$$

$$= [OH^-]_f + K_1[OH^-][Cu(OH)_2(H_3IO_6)_2]^{3-} + \frac{K_1K_2[Cu(OH)_2(H_3IO_6)_2]^{3-}[OH^-]}{[H_2IO_6^{3-}]}$$

$$+ \frac{K_1K_2K_3[Cu(OH)_2(H_3IO_6)_2]^{3-}[OH^-][L\text{-}CYS]}{[H_2IO_6^{3-}]}. \quad (A.5)$$

The view of low concentrations of DPC used, the second, third and fourth terms in the above equation are neglected, therefore,

$$[OH]_t = [OH]_f, \quad (A.6)$$

$$[L\text{-}CYS]_t = [L\text{-}CYS]_f. \quad (A.7)$$

Substituting equitation's (A.3), (A.6), and (A.7) in (A.1) we get

$$\text{Rate} = \frac{kK_1K_2K_3[L\text{-}CYS][OH^-][DPC]}{[H_2IO_6^{3-}] + K_1K_2K_3[OH^-][L\text{-}CYS] + K_1K_2[OH^-] + K_1[H_2IO_6^{3-}][OH^-]}.$$

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