



Autocatalyzed oxidation of amino acid, L-Citrulline by diperiodatocuprate(III) complex in aqueous alkaline medium: a kinetics and mechanistic approach

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Abstract. Autocatalysed oxidation of important amino acid, L-Citrulline(L-Cit) by coordination complex, diperiodatocuprate(III) in aqueous alkaline medium at a constant ionic strength of 0.05 mol dm^{-3} was studied spectrophotometrically. Autocatalysis was observed by one of the products formed, i.e., Cu (II). 1:4 stoichiometry (L-Cit:DPC) exhibited between the reaction of L-Cit and DPC in aqueous alkaline medium. The path is of first-order in [DPC], less than unit order in [L-Cit] and independent in [OH⁻]. Periodate has a retarding effect on the rate of reaction. Ionic strength has a negligible effect on the reaction rate. The main reaction products were identified by spot tests and spectroscopic analysis. A composite mechanism involving uncatalysed and an autocatalysed reaction path (*via* free radical) was proposed. The activation parameters for the slow step of the mechanism and also the thermodynamic quantities for different steps of the mechanism were determined and discussed.

Keywords. Kinetics; mechanism; diperiodatocuprate(III); L-citrulline; autocatalysis.

1. Introduction

Autocatalytic processes are crucial of the mechanisms leading to the symmetry breaking of chemical compounds towards homochirality^{1,2} and identified in several experimental systems.^{3,4} Catalytic oxidation of several substrates by various different oxidants is reported.^{5,6} Oxidation of various biological substrates and polyphenol by air oxygen catalysed by Cu²⁺ and Fe²⁺ complexes exhibit transient oscillations.^{7,8}

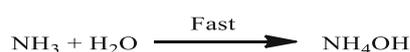
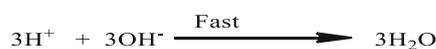
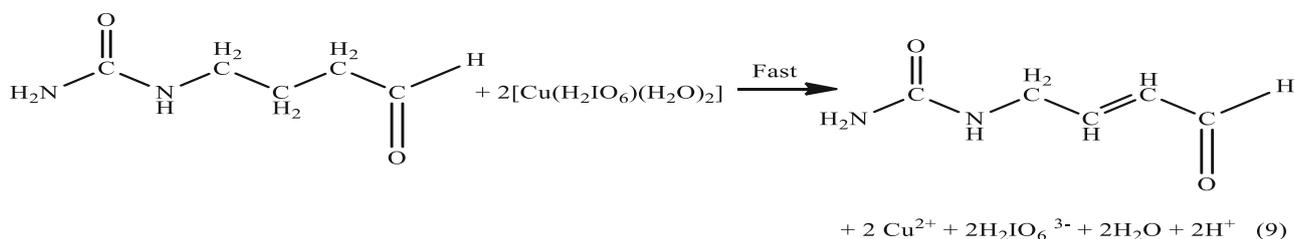
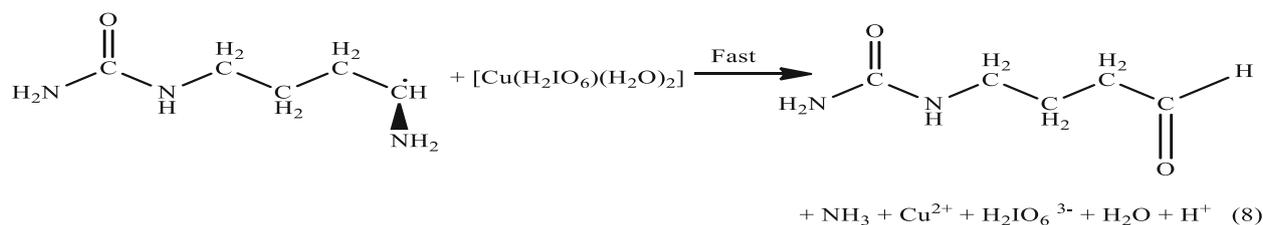
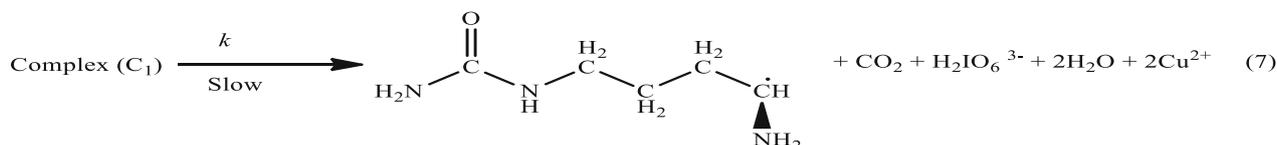
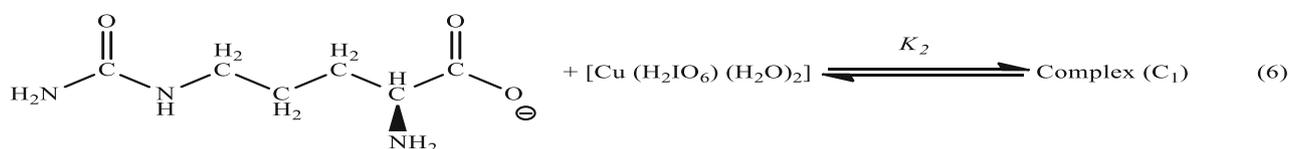
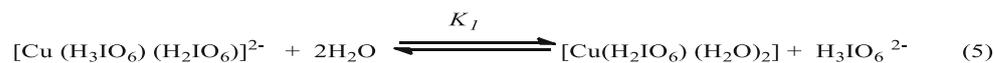
The study of the metals in their highest oxidation state has fascinated many researchers in current years. Such transition metals can be stabilized by chelating with suitable bi or polydentate ligands. Diperiodatocuprate(III) (DPC) is an excellent oxidant due to its restricted solubility and stability in aqueous medium. The reactivity of a few alcohols with diperiodatocuprate(III) (DPC)⁹ is reported by Movius. The characterization, structural determination and synthesis of DPC have been reported.^{10,11} Copper periodate complexes in their +3 oxidation state have been

widely used in the examination of several organic compounds.¹² The oxidation reactions by DPC studies are reported.¹³ Complexes of copper have occupied a major role in oxidation chemistry due to their profusion and relevance in biological chemistry.¹⁴ In the copper(II) catalyzed oxidation of various amino acids by peroxy, disulphate involves copper(III) as an intermediate.¹⁵ DPC is a versatile one-electron oxidant and involves multiple equilibria between different copper(III) species. Hence, it can be a matter of intrigue to many researchers to know which of the active species of the copper(III) is involved in the reaction.

Human kidney converts L-Citrulline (L-Cit) into another important amino acid called L-arginine and oxide of nitrogen. In the human body, L-Cit boosts the production of nitric oxide. Oxide of nitrogen (nitric oxide) helps arteries to relax and work better, which also regulates the flow of blood throughout the body. It is used in the treatment of Parkinson's disease and certain dementias. The human body needs certain

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Scheme 1. Mechanism for the oxidation of L-Cit by alkaline DPC.

proteins. L-Cit helps to increase the required supply of ingredients. L-Cit is a key intermediate compound in the urea cycle. In the body, L-Cit is produced as a byproduct of the enzymatic production of nitric oxide from the amino acid arginine, catalyzed by nitric oxide synthase.¹⁶

In many of the cases, amino acids are oxidised through decarboxylation and deamination.¹⁷ The oxidation of amino acids is of interest as the oxidation products differ for different oxidants.^{18,19} Such oxidation studies may throw some light on the mechanism of conversion of amino acid in the biological system.

Kinetics and mechanistic study of L-Cit by permanganate in acidic and basic media have been reported.²⁰ In basic media, order with respect to [permanganate] and [L-Cit] is unity, whereas less than

unity is [alkali]. Rate of reaction is increased with an increase in ionic strength. In the present kinetics and mechanistic study of L-Cit by DPC, the order with respect to DPC, L-Cit is unity and less than unity, respectively. Rate is independent of $[\text{OH}^-]$ and ionic strength. The retarding effect of periodate on rate is observed. One more interesting fact is that the autocatalysis of Cu(II) was observed.

In view of the observed study of autocatalysis by Cu(II) in the oxidation of L-Cit by DPC and of interest to study mechanism of oxidation L-Cit by Cu(III) complex in aqueous alkaline medium, L-Cit as a substrate for oxidation has been selected. The title reaction represents a full mechanistic and kinetic oxidation of L-Cit by DPC in alkali media to establish the optimum conditions affecting such oxidation

reactions. To understand more about the active species of the reactants in these media, and finally to determine the plausible oxidation mechanisms on the basis of the observed kinetic, spectral studies were taken up. By understanding the mechanism, the reactivity of L-Cit towards DPC could be interpreted and understood.

2. Experimental

2.1 Materials and reagents

Reagent grade chemicals and double distilled water were used throughout the experimental work. The required solution of L-Cit (S D fine-CHEM Ltd., Mumbai, India) was prepared by dissolving the appropriate amount of sample in double-distilled water. The diperiodatocuprate(III) compound was prepared²¹ and standardized through the standard procedure.^{22a} The UV-vis spectral study revealed that the maximum absorption peak at 418 nm verified the existence of copper(III) complex. Periodate solution was prepared by dissolving the appropriate amount of periodate sample in hot water and kept for 24 h to attain the equilibrium. Its concentration was determined iodometrically²³ at neutral pH maintained using phosphate buffer. The Cu(II) solution was made by dissolving the known amount of copper sulphate (BDH) in double-distilled water. KOH (BDH) and KNO₃ (AR) were employed to maintain the required alkalinity and ionic strength, respectively. The constant temperature within ± 0.1 °C range was maintained unless otherwise stated.

2.2 Kinetics measurements

Kinetic measurements were carried out by using a Peltier accessory for temperature control attached to Varian CARY 50 Bio UV-vis Spectrophotometer (Varian, Victoria-3170, Australia). For pH measurement, an Elico pH meter model LI 120 was used. For product analysis, the liquid chromatography (LC) technique (Acquity UPLC) mass spectrometry (MS) instrument, SynaptG2 and FTIR technique: Nicolet-5700 USA, were used.

Kinetic runs were performed under pseudo-first-order ($[L-Cit] \gg [DPC]$) at 25 ± 0.1 °C conditions. The required amount previously thermostatted solution of L-Cit and DPC were used to initiate the reaction, to which required a concentration of KNO₃, KOH and KIO₄ were also added to maintain reaction conditions. The progression of the reaction was studied spectrophotometrically at 418 nm, by recording the decrease in absorbance due to DPC with the molar absorptivity index, $\epsilon = 6240 \pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Literature $\epsilon = 6230$).²⁴ The negligible interference of other species present were observed in the reaction mixture at this wavelength. The log (Abs) versus time plots were made to calculate the pseudo-

first-order rate constants, ' k_{obs} ' and they were linear up to 30% of the completion of the reaction under the range of $[OH^-]$ used. Above 30% of completion of the reaction, a non-linearity was due to the autocatalysis, by copper(II) and the rate constants were reproducible about $\pm 5\%$. During the kinetics, a constant ($5.0 \times 10^{-5} \text{ mol dm}^{-3}$) concentration of KIO₄ was used throughout the study unless otherwise stated. Since the excess amount of periodate was present in DPC, the probability of oxidation of L-Cit by periodate in an alkaline medium at 25 °C was tested. Iodometrically, the progression of reaction was studied. However, it was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of L-Cit.

The total $[OH^-]$ and $[IO_4^-]$ were calculated by the consideration of previously present ions in the DPC solution and that additionally added. No effect of added carbonate was observed on the rate of reaction. The spectral change of reaction progression has been shown in Figure 1A, in which a decrease in $[DPC]$ at 418 nm during the reaction was observed. The autocatalysed oxidation of Cu(II) is also

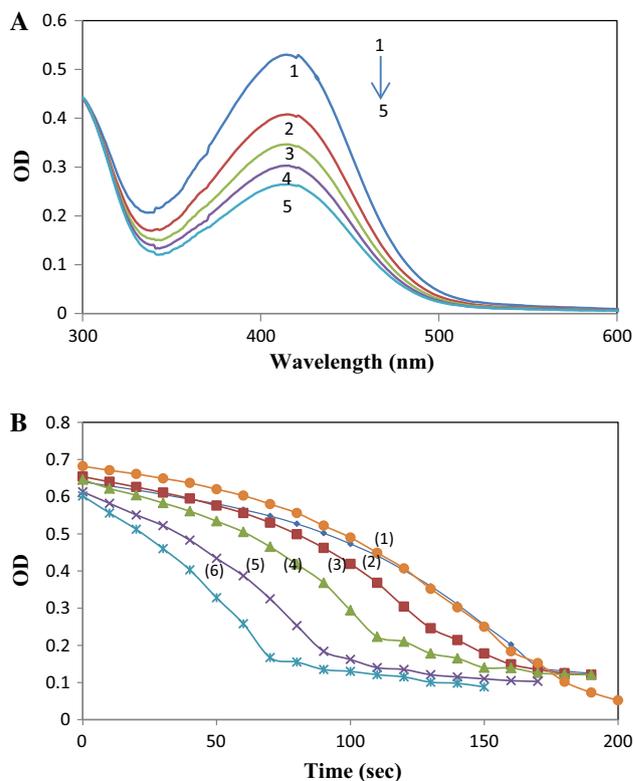


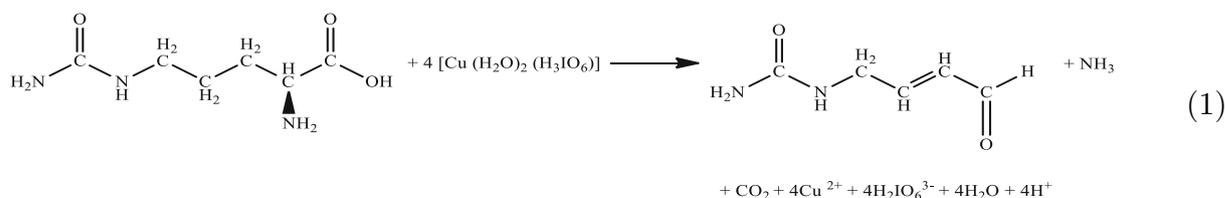
Figure 1. (A) Spectroscopic changes of DPC during the reaction period in the Cu(II) autocatalysed oxidation of L-Cit by diperiodatocuprate(III) at 25 °C (scanning interval 30 s). $[DPC] = 1.0 \times 10^{-4}$, $[OH^-] = 0.02$, $[L-Cit] = 1.0 \times 10^{-3}$, $I = 0.05 \text{ mol dm}^{-3}$. (B) Autocatalysis of Cu(II) on oxidation of L-Cit by alkaline DPC at 25 °C at various $[Cu(II)]$. $[DPC] = 1.0 \times 10^{-4}$, $[L-Cit] = 1.0 \times 10^{-3}$, $[OH^-] = 0.02$, $[IO_4^-] = 5.0 \times 10^{-5}$, $I = 0.05$, and $Cu(II) =$ (1) without Cu(II) (2) (2×10^{-6}), (3) (4×10^{-6}), (4) (6×10^{-6}), (5) (8×10^{-6}), (6) (10×10^{-6})/ mol dm^{-3} .

shown in Figure 1B. Microsoft 2007 Excel program was used for regression analysis of experimental data, standard deviation 'S' and regression coefficient 'r' of points.

3. Results and Discussion

3.1 Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPC to L-Cit in the presence of the constant amount of OH⁻, KNO₃ and KIO₄ were kept for 4 h in a closed vessel under nitrogen atmosphere. The unreacted DPC was estimated spectrophotometrically at 418 nm. The results indicated a 1:4 stoichiometry (L-Cit:DPC) as given in equation (1).



The above stoichiometric equation is consistent with the results of product analysis. The main reaction product was identified as the corresponding aldehyde, which was confirmed by LC-MS spectral studies (Figure S1, Supplementary Information) and spot test.²⁵ The mass spectrum showed molecular ion peak at m/z 128 and IR absorption frequency peaks at carbonyl 1728 cm⁻¹ and aldehyde -CH 2823 cm⁻¹, 2728 cm⁻¹ confirming the product of (E)-1-(4-oxobut-2-en-1-yl)urea. All other peaks observed in LC-MS and IR can be interpreted as per the observed structure of the product. Another by-product, ammonia was detected by Nessler's reagent.^{22b} Brisk effervescence was observed when the product was treated with dil HCl which confirmed the byproduct CO₂.²⁶ Cu(II) was detected by its UV-vis spectrum. The intermediate product [4-(carbamoylamino) butyraldehyde] obtained was same as that obtained by the oxidation of L-Cit in earlier works.²⁰ The reaction products did not undergo further oxidation under the present kinetic conditions. Test for the corresponding acid was negative.

3.2 Reaction orders

The log k_{obs} vs. log concentration plots were used to find the order of reaction with respect to [L-Cit], [OH⁻] and [IO₄⁻]. Further, the differential method was used to

confirm the orders by the plot log (initial rate) vs. log (concentration) applying the equation log (rate) = log $k + n \log c$. These orders were obtained by varying the concentrations of L-Cit, alkali and periodate in turn while keeping all other concentrations and conditions constant.

3.3 Effect of diperiodatocuprate (III)

The DPC concentration varied in the range of 2.0×10^{-5} to 2.0×10^{-4} mol dm⁻³, with other constant concentration of L-Cit, 1.0×10^{-3} mol dm⁻³, alkali, 2.0×10^{-2} mol dm⁻³, and a constant ionic strength 0.05 mol dm⁻³; the non-variation in the pseudo-first-order rate constants at various

concentrations of DPC indicates the order in [DPC] as unity (Table 1). This was also confirmed from the linearity and parallelism of log (concentration) versus time plots up to 30% completion of the reaction.

3.4 Effect of L-Citrulline

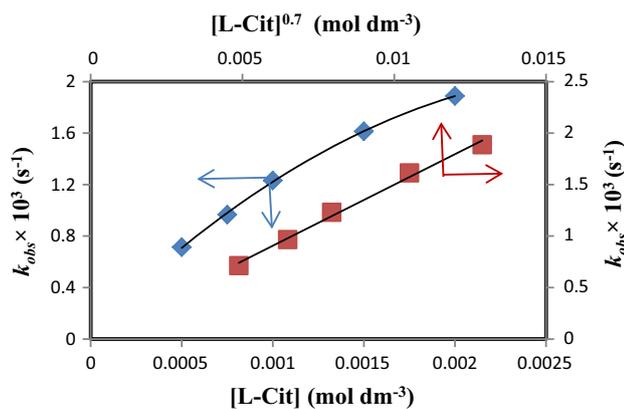
The concentration of L-Cit was varied in the range 0.5×10^{-3} to 2.0×10^{-3} mol dm⁻³ at 25 °C while maintaining all other reactant concentrations and conditions constant. The rate constant (k_{obs}) values increased with the increase in the concentration of L-Cit, indicating an evident less than unit order dependence on [L-Cit] ($r \geq 0.995$, $S \leq 0.027$) (Table 1) under the concentrations of experiments carried out. The less than unit order in [L-Cit] was confirmed by the linearity of the plot of k_{obs} vs [L-Cit]^{0.7} rather than the plot of k_{obs} vs [L-Cit] (Figure 2).

3.5 Effect of alkali

The effect of [OH⁻] was performed by varying the concentration from 0.2×10^{-2} to 2.0×10^{-2} mol dm⁻³ while keeping all other concentrations of reactants constant. It was observed that OH⁻ has no effect on the rate of reaction.

Table 1. Effects of [DPC], [L-Cit], [OH⁻] and [IO₄⁻] on oxidation of L-Cit by DPC in alkaline medium at 25 °C, I = 0.05 mol dm⁻³.

[DPC] × 10 ⁴ (mol dm ⁻³)	[L-Cit] × 10 ³ (mol dm ⁻³)	[OH ⁻] × 10 ² (mol dm ⁻³)	[IO ₄ ⁻] × 10 ⁴ (mol dm ⁻³)	$k_{obs} \times 10^3$ (S ⁻¹)	
				Expt. ^a	Calcd. ^a
0.2	1.0	2.0	0.5	1.25	1.23
0.5	1.0	2.0	0.5	1.27	1.23
1.0	1.0	2.0	0.5	1.23	1.23
1.5	1.0	2.0	0.5	1.25	1.23
2.0	1.0	2.0	0.5	1.22	1.23
1.0	0.5	2.0	0.5	0.71	0.70
1.0	0.75	2.0	0.5	0.96	0.97
1.0	1.0	2.0	0.5	1.23	1.29
1.0	1.5	2.0	0.5	1.61	1.78
1.0	2.0	2.0	0.5	1.88	2.20
1.0	1.0	0.2	0.5	1.26	1.23
1.0	1.0	0.4	0.5	1.28	1.23
1.0	1.0	0.8	0.5	1.25	1.23
1.0	1.0	1.0	0.5	1.23	1.23
1.0	1.0	2.0	0.5	1.26	1.23
1.0	1.0	2.0	0.1	3.91	3.58
1.0	1.0	2.0	0.2	2.53	2.48
1.0	1.0	2.0	0.5	1.23	1.29
1.0	1.0	2.0	0.8	0.87	0.87
1.0	1.0	2.0	1.0	0.73	0.71

^aExperimental and calculated values.**Figure 2.** Plot of k_{obs} versus $[L-Cit]^{0.7}$ and k_{obs} versus $[L-Cit]$.

3.6 Effect of periodate

The effect of [IO₄⁻] was performed by varying the concentration from 0.1 × 10⁻⁴ to 1.0 × 10⁻⁴ mol dm⁻³ while keeping all other concentrations of reactants constant. It was found that the added periodate retarded the rate, with inverse fractional order in periodate (Table 1).

3.7 Effect of initially added products

The initially added product, copper(II) was studied in the range 1.0 × 10⁻⁶ to 1.0 × 10⁻⁵ mol dm⁻³ while

keeping all other concentrations of reactants constant. The initially added Cu(II) increased the rate of reaction (Table 2) with an order +0.3 (Figure 3), which was an interesting result.

Hence, the experimental rate law for the reaction is given by

$$\text{Rate} = k_{obs}[\text{DPC}]^1[\text{L-Cit}]^{0.7}[\text{IO}_4^-]^{-0.7}[\text{Cu(II)}]^{0.3}$$

3.8 Effect of ionic strength (I)

The addition of KNO₃, at constant [L-Cit], [DPC], [OH⁻] and [IO₄⁻] was found to have no effect on the rate of reaction with an increase in ionic strength.

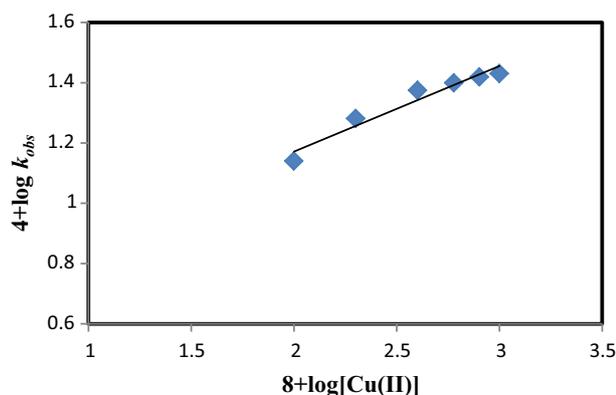
3.9 Test for free radicals (polymerization)

The intervention of free radicals in the reaction was examined as follows: The reaction mixture with standard conditions was mixed with organic compound, acrylonitrile monomer and kept for 2 h, under nitrogen atmosphere. The reaction was further diluted with methanol; a white precipitate was observed, confirming the intervention of free radicals in the reaction. The blank experiment of DPC and acrylonitrile (or

Table 2. Effect of Cu(II), on oxidation of L-Cit by alkaline DPC.

[Cu(II)] × 10 ⁶ (mol dm ⁻³)	<i>k</i> _{obs(autocat)} × 10 ³ (s ⁻¹)	<i>k</i> _{cal(autocat)} × 10 ³ (s ⁻¹)
1.0	1.38	1.38
2.0	1.91	1.89
4.0	2.37	2.32
6.0	2.51	2.52
8.0	2.62	2.60
10.0	2.69	2.70

[DPC] = 1.0 × 10⁻⁴; [L-Cit] = 1.0 × 10⁻³; [OH⁻] = 0.02; [IO₄⁻] = 5.0 × 10⁻⁵;
I = 0.05/mol dm⁻³.

**Figure 3.** Order plot of 4 + log *k*_{obs} against 8 + log [Cu(II)].

L-cit and acrylonitrile) did not induce any polymerization under the same conditions as those induced for the mixture of reaction. Initially added acrylonitrile decreased the rate of reaction, indicating free radical intervention, which was the case in earlier work.²⁷

3.10 Effect of temperature

The rate of reaction was measured for every 5 K raise in the temperature (283, 288, 293, 298, 303/K) at varying [L-Cit] and [IO₄⁻]. The reaction rates were increased with an increase in temperatures (Table 3A). The slope of the plot of log *k* vs. 1/*T* (*r* ≥ 0.998) was used to calculate the energy of activation and other activation parameters (Table 3B).

3.11 Discussion of mechanism

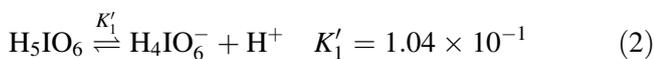
The [Cu(HIO₆)₂(OH)₂]⁷⁻²⁸ has been reported as water-soluble copper(III) periodate complex in an aqueous alkaline medium. However, studies at a higher pH range employed showed that periodate is unexpected to exist as HIO₆⁴⁻ (as present in the complex) as is clear from its involvement in the multiple equilibria²⁹ ((2)–

Table 3. Effect of temperature on Cu(II) autocatalysed oxidation of L-Cit by diperiodatocuprate(III) with respect to the slow step of Scheme 1.

Temperature (K)	<i>k</i> × 10 ³ (s ⁻¹)	
(A) Effect of temperature		
283	3.75	
288	4.82	
293	6.25	
298	7.66	
303	9.58	
(B) Activation parameters		
E _a (kJ mol ⁻¹)	38.9 ± 1.4	
ΔH [#] (kJ mol ⁻¹)	36.1 ± 3.2	
ΔS [#] (J K ⁻¹ mol ⁻¹)	-156 ± 6	
ΔG [#] (kJ mol ⁻¹)	82 ± 6	
log A	4.6 ± 0.1	
Temperature	10 ⁶ <i>K</i> ₁ (mol dm ⁻³)	10 ³ <i>K</i> ₂ (dm ³ mol ⁻¹)
(C) Effect of temperature to calculate <i>K</i> ₁ and <i>K</i> ₂ for the oxidation of L-Cit by diperiodatocuprate(III) in aqueous alkaline medium.		
283	4.5 ± 0.1	2.3 ± 0.2
288	4.2 ± 0.2	2.7 ± 0.2
293	2.5 ± 0.3	4.3 ± 0.3
298	1.9 ± 0.2	5.5 ± 0.4
303	0.8 ± 0.1	11.5 ± 0.2
Thermodynamic quantities	Values from <i>K</i> ₁	Values from <i>K</i> ₂
(D) Thermodynamic quantities using <i>K</i> ₁ and <i>K</i> ₂		
ΔH (kJ mol ⁻¹)	-71 ± 3	56 ± 3
ΔS (JK ⁻¹ mol ⁻¹)	-301 ± 8	259 ± 6
ΔG ₂₉₈ (kJ mol ⁻¹)	32.0 ± 0.2	-21.7 ± 0.4

(4)) depending upon pH of the solution. Periodic acid exists as H₄IO₆ at pH 7 and as H₅IO₆ in acid medium. Thus, in the present study in alkaline medium, H₃IO₆²⁻ and H₂IO₆³⁻ are found to be the main active species. Periodate dimerizes³⁰ at higher concentration. However, in the present kinetic conditions, the formation of such species is negligible. Thus, [Cu(H₃IO₆)(H₂IO₆)²⁻] is the soluble copper(III) periodate complex

in the employed pH conditions, also supported by the earlier work.²⁷



The results obtained in the present study were entirely different from the earlier work on DPC oxidation.³¹ Further kinetic studies were made in order to check the active species of DPC in such alkaline media. It was observed that the reaction exhibited an order of negative fractional with respect to $[\text{IO}_4^-]$, less than unit order in $[\text{L-Cit}]$ and it is independent of alkali concentrations (Table 1). In view of the retarding effect of periodate, the active species of DPC has been proposed as $[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2]$ which was also observed in earlier report³² and the mechanism befitting the obtained results was proposed (Scheme 1).

In aqueous alkaline medium, diaquomonoperiodato copper(III) complex (MPC) [in Eq. (5)] was produced due to the substitution of bidentate ligand $[\text{H}_3\text{IO}_6^{2-}]$ of DPC by water molecules and its formation was important in the present study. The kinetics and mechanistic study of oxidation by silver(III) and Nickel(IV) periodate complexes^{33,34} also reported similar form of complexes.

In an aqueous medium, the Zwitter ion form of L-Cit has been reported.³⁵ L-Cit exists as the protonated form in highly acidic medium whereas fully deprotonated form in highly basic medium.³⁵ Based on the kinetic measurements, the reaction was of first order with respect to DPC, negative fractional order with respect to periodate, independent of alkali, fractional-order in $[\text{L-Cit}]$ and acrylonitrile test revealed reaction involving free radical. The DPC species reacted with substrate (L-Cit) in its deprotonated form to give a complex (C_1) between the Cu(III) species and L-Cit and its confirmation was obtained from UV spectral study of DPC ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$), L-Cit ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$), alkali (0.02 mol dm^{-3}) and mixture of both. A hypsochromic shift from 418 nm to 414 nm in the spectra of DPC was observed (Figure S2, Supplementary Information). Further, this complex decomposed to give a free radical derived from decarboxylated L-Cit in a slow step. Thus, formed free radical reacted with three moles are of DPC in succeeding steps to give the main product. The

other products, Cu(II), periodate and ammonia are shown in (Scheme 1).

The formation of a complex between DPC and L-Cit has been proved by Michaelis-Menten plot, which confirmed that less than unit order with respect to $[\text{L-Cit}]$. Such type of complex between a substrate and oxidant has been reported in earlier studies.³⁶ Scheme 1 lead to rate law (10).

$$k_{obs} = \frac{\text{Rate}}{[\text{DPC}]} = \frac{kK_1K_2[\text{L-Cit}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 + K_1K_2[\text{L-Cit}]} \quad (10)$$

This explains all the observed kinetic orders of different species. The rate law eq. (10) was rearranged to eq. (11), which is suitable for verification.

$$\frac{1}{k_{obs}} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_1K_2[\text{L-Cit}]} + \frac{1}{kK_2[\text{L-Cit}]} + \frac{1}{k} \quad (11)$$

From eq. (11), the plots of $1/k_{obs}$ versus $1/[\text{L-Cit}]$ ($r \geq 0.997$, $S \leq 0.013$) and $1/k_{obs}$ versus $[\text{H}_3\text{IO}_6^{2-}]$ ($r \geq 0.998$, $S \leq 0.015$) should be linear and were found to be so (Figure 4), while other terms being

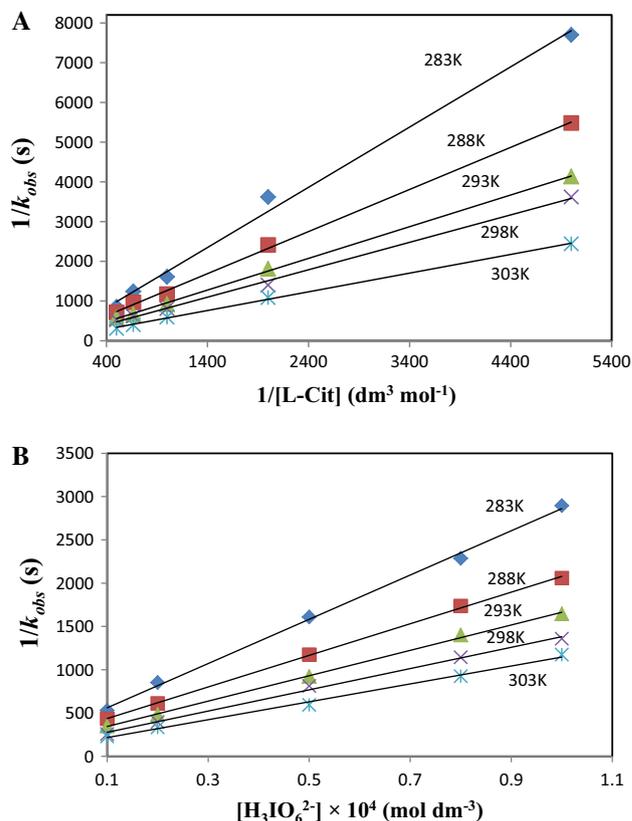


Figure 4. Verification of rate law (10) in the form of eq. (11) for the oxidation of L-Cit by diperiodato-cuprate(III). Plots of (A) $1/k_{obs}$ versus $1/[\text{L-Cit}]$, (B) $1/k_{obs}$ versus $[\text{H}_3\text{IO}_6^{2-}]$, at various temperatures (conditions as in Table 1).

constant. The values of constants, K_1 , K_2 , and k as $(1.9 \pm 0.2) \times 10^{-6} \text{ mol dm}^{-3}$, $(5.55 \pm 0.1) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ and $(7.6 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$, respectively were calculated from slopes and intercepts of such plots. These reaction constants were in good agreement with earlier works.³⁷ Further, these constants were used to replicate the k_{obs} for different experimental conditions. The k_{cal} and k_{obs} were fairly in agreement with each other, which consolidated the mechanism.

For the 1st and 2nd equilibrium steps (Scheme 1), the thermodynamic extents can be determined as follows. The [L-Cit] and $[\text{H}_3\text{IO}_6^{2-}]$ (as in Table 1) were varied at five different temperatures (283, 288, 293, 298, 303/K). The plots of $1/k_{obs}$ versus $1/[\text{L-Cit}]$ and $1/k_{obs}$ versus $[\text{H}_3\text{IO}_6^{2-}]$ should be linear which are found to be so in Figure 4. The values of K_1 , K_2 and k_1 were calculated with the help of slopes and intercepts of such plots, at different temperatures. These values are shown in Table 3A. The plot of $\log K_1$ versus $1/T$ ($r \geq 0.9824$, $S \leq 0.007$) was taken into consideration for variation of K_1 with temperature i.e., Vant Hoff's plot and the values of enthalpy of reaction ΔH , entropy of reaction ΔS and free energy of reaction ΔG , were calculated for the first and second equilibrium steps. These values so obtained are shown in Table 3D. These values are compared with those obtained for the slow step of the reaction ($\Delta H^\ddagger = 36.1 \text{ kJ mol}^{-1}$) which shows that these values mainly refer to the rate-limiting step, supporting the fact that the reaction before the rate-determining step is fairly fast and involves low activation energy ($\Delta H = 71.3 \text{ kJ mol}^{-1}$).³⁶

The values of ΔH^\ddagger and ΔS^\ddagger were both commendatory for transfer of electron processes, the complex (C_1) is more ordered than the reactants due to negative value of ΔS^\ddagger .³⁸ The observed adequate activation energy and considerable entropy of activation supports a complex transition state in the reaction.³⁹ The principle of non-complementary oxidations taking place in the sequence of one-electron steps suits Scheme 1. The reaction between the L-Cit and DPC would furnish a radical intermediate. Similar such radical intermediate has also been observed in earlier works.^{36,40} The independence of rate of reaction on ionic strength is due to the participation of non-ionic species like MPC in the rate-determining step (Scheme 1).

3.12 Autocatalysis

The autocatalysis by one of the products, Cu(II), is interesting. The first order in [DPC] and less than

unity in [L-Cit] are observed. The apparent less than unit order in Cu(II) ion may be assigned to complex formation between L-Cit and Cu(II). Further complex C_2 will then subsequently interact with MPC. These steps are shown in Scheme 2, which will form a part of Scheme 1. The plot of $1/k_{obs}$ vs. $1/[\text{Cu(II)}]$ was a linear and hypsochromic shift of Cu(II) from 763 nm to 755 nm in presence of L-Cit are the confirmation for complex formation between L-Cit and Cu^{2+} .

The rate law for autocatalysed oxidation of L-Cit by DPC is given by equation (14)

$$\text{Rate} = \frac{k_a K_3 [\text{DPC}] [\text{L-Cit}]_T [\text{Cu}^{2+}]_T}{\{1 + K_3 [\text{Cu}^{2+}]\} \times \{1 + K_3 [\text{L-Cit}]\}} \quad (14)$$

Or

$$\begin{aligned} k_{\text{auto(cat)}} &= \frac{\text{Rate}}{[\text{DPC}]} \\ &= \frac{k_a K_3 [\text{L-Cit}]_T [\text{Cu}^{2+}]_T}{1 + K_3 [\text{L-Cit}] + K_3 [\text{Cu}^{2+}] + K_3^2 [\text{Cu}^{2+}] [\text{L-Cit}]} \end{aligned} \quad (15)$$

Hence, when $[\text{Cu}^{2+}]$ is initially present, a combination scheme involving steps of Schemes 1 and 2 operated

$$\begin{aligned} k_{\text{Total}} &= k_{obs} + k_{\text{auto(cat)}} \\ k_{\text{Total}} &= \frac{k K_1 K_2 [\text{L-Cit}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 + K_1 K_2 [\text{L-Cit}]} \\ &+ \frac{k_a K_3 [\text{L-Cit}]_T [\text{Cu}^{2+}]_T}{1 + K_3 [\text{L-Cit}] + K_3 [\text{Cu}^{2+}] + K_3^2 [\text{Cu}^{2+}] [\text{L-Cit}]} \end{aligned}$$

For auto catalysed part, the eq. (15) only contributes.

On rearranging equation (15), we get

$$\frac{[\text{L-Cit}]}{k_{\text{auto(cat)}}} = \frac{1}{k_a K_3 [\text{Cu}^{2+}]} + \frac{1}{k_a} + \frac{[\text{L-Cit}]}{k_a [\text{Cu}^{2+}]} + \frac{K_3 [\text{L-Cit}]}{k_a} \quad (16)$$

According to equation (16), the plot of $[\text{L-Cit}]/k_{\text{auto(cat)}}$ vs. $1/[\text{Cu(II)}]$ should be linear and was found to be so (Figure 5). ($r > 0.9755$, $s > 0.0224$). The slope and intercept of such plot lead to the values of K_3 and k_a as $8.41 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ and $2.56 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. Using these values, $k_{\text{auto(cat)cal}}$ under various conditions were calculated. There is a reasonable agreement between the experimental and calculated rate constants (Table 2).

was identified as (E)-1-(4-(2-ethyl-1-yl)urea by LCMS and IR spectroscopic analysis.

Supplementary Information (SI)

All additional information pertaining to the main reaction product (Figure S1) and spectroscopic evidence for the complex formation between DPC and L-Cit (Figure S2) and the Appendix to Scheme 1 are available at www.ias.ac.in/chemsci.

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