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Mechanistic aspects of uncatalyzed and ruthenium(III) catalyzed oxidation of DL-ornithine by copper(III) periodate complex in aqueous alkaline medium: A comparative kinetic study

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ABSTRACT

The oxidation of DL-ornithine monohydrochloride (OMH) by diperiodatocuprate(III) (DPC) has been investigated both in the absence and presence of ruthenium(III) catalyst in aqueous alkaline medium at a constant ionic strength of 0.20 mol dm^{-3} spectrophotometrically. The stiochiometry was same in both the cases, i.e., [OMH]/[DPC] = 1:4. In both the catalyzed and uncatalyzed reactions, the order of the reaction with respect to [DPC] was unity while the order with respect to [OMH] was < 1 over the concentration range studied. The rate increased with an increase in [OH$^-$] and decreased with an increase in [IO$_4{}^-$] in both cases. The order with respect to [Ru(III)] was unity. The reaction rates revealed that Ru(III) catalyzed reaction was about eight-fold faster than the uncatalyzed reaction. The oxidation products were identified by spectral analysis. Suitable mechanisms were proposed. The reaction constants involved in the different steps of the reaction mechanisms were calculated for both cases. The catalytic constant (K_C) was also calculated for catalyzed reaction at different temperatures. The activation parameters with respect to slow step of the mechanism and also the thermodynamic quantities were determined. Kinetic experiments suggest that [Cu(H$_2$IO$_6$)(H$_2$O)$_2$] is the reactive copper(III) species and [Ru(H$_2$O)$_5$OH]$^{2+}$ is the reactive Ru(III) species.

1. Introduction

Ornithine is a non-protein amino acid [1], derived from the breakdown of arginine during the citric acid cycle. It helps to build muscle and reduce body fat, especially when combined with the amino acids arginine and carnitine. It is also needed for the formation of citrulline, proline and glutamic acid. Ornithine helps to remove toxic ammonia from the liver, and reduce the effects of cirrhosis of the liver and disorders associated with liver malfunction. Ornithine is the major source of polyamines in mammalian physiological systems [2]. Increased urinary polyamine levels have been demonstrated in humans with varied types of cancers. The metabolism of DL-[1-^{14}C] ornithine monohydrochloride in rats with either Walker 256 carcinoma or chemically induced methylcholanthrene tumors was studied, whose attempts showed to develop ornithine as a biological marker of cancer [3,4].

Transition metals in their higher oxidation states can generally be stabilized by chelation with suitable polydentate ligands. These metal chelates such as diperiodatocuprate(III) [5], diperiodatoargentate(III) [6] and diperiodatonickelate(IV) [7] are good oxidants in a medium with an appropriate pH value. Diperiodatocuprate(III) is a versatile one-electron oxidant and the oxidation study of DPC is scanty in view of its limited solubility and stability in aqueous medium. Its use as an analytical reagent is now well recognized [8]. Copper complexes have a major role in oxidation chemistry due to their abundance and relevance in biological chemistry [9–11]. Copper(III) is involved in many biological electron transfer reactions [12]. When copper(III) periodate complex is the oxidant and multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is the active oxidant.

Transition metals are known to catalyze many oxidation–reduction reactions since they involve multiple oxidation states. In recent years the use of transition metal ions such as ruthenium, osmium, palladium, manganese, chromium, iridium, either alone or as binary mixtures, as catalysts in various redox processes have attracted considerable interest [13]. Ru(III) acts as catalyst in the oxidation of many organic and inorganic substrates [14,15]. Although the mechanism of catalysis depends on the nature of the substrate, oxidant and experimental conditions, it has been shown [16] that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. Ruthenium(III) catalysis in redox reactions

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involves different degrees of complexity, due to the formation of different intermediate complexes and different oxidation states of ruthenium.

Literature survey revealed that no attention has been paid towards the oxidation of DL-ornithine monohydrochloride [(±)-2,5-diaminopentanoic acid monohydrochloride] with any oxidant from the kinetic and mechanistic point of view. It is also observed that, no one has examined the role of any catalyst on the oxidation of this ubiquitous amino acid. We have observed that ruthenium(III) in micro amounts catalyzes the oxidation of OMH by DPC in alkaline medium. Such studies are of much significance in understanding the mechanistic profile of ornithine in redox reactions and provide an insight into the interaction of metal ions with the substrate and its mode of action in biological systems. Also to know the active species of Cu(III) and catalyst Ru(III), and the complexity of the reaction, a detailed study of the title reaction becomes important. Hence, the present investigation is aimed at checking the reactivity of OMH towards DPC in both uncatalyzed and ruthenium(III) catalyzed reactions and to arrive at the plausible mechanisms.

2. Experimental

2.1. Chemicals and solutions

All reagents were of analytical reagent grade and Millipore water was used throughout the work. A solution of DL-ornithine monohydrochloride (HiMedia Laboratories) was prepared by dissolving an appropriate amount of recrystallized sample in Millipore water. The purity of OMH was checked by comparing its IR spectrum with the literature data and with its m.p. 232–234 °C. The required concentration of OMH was obtained from its stock solution. A standard stock solution of Ru(III) was prepared by dissolving $RuCl_3$ (S.D. Fine Chem.) in 0.20 mol dm^{-3} HCl. The concentration was determined [17,18] by EDTA titration.

The copper(III) periodate complex was prepared [19,20] and standardized by a standard procedure [21]. The UV–vis spectrum with maximum absorption at 415 nm verified the existence of copper(III) complex. The ionic strength was maintained by adding KNO_3 (AR) solution and the pH value was regulated with KOH (BDH) solution. A stock solution of IO_4^- was prepared by dissolving a known weight of KIO_4 (Riedel-de-Hean) in hot water and used after keeping for 24 h to attain the equilibrium. Its concentration was ascertained iodometrically [22], at neutral pH maintained using phosphate buffer. The pH of the medium in the solution was measured by ELICO (LI120) pH meter. Solutions of OMH and DPC were always freshly prepared before use.

2.2. Instruments used

(i) For kinetic measurements, a Peltier Accessory (temperature control) attached Varian CARY 50 Bio UV-vis Spectrophotometer (Varian, Victoria-3170, Australia) connected to a rapid kinetic accessory (HI-TECH SFA-12) was used.
(ii) For product analysis, a QP-2010S Shimadzu gas chromatograph mass spectrometer, Nicolet 5700-FT-IR spectrometer (Thermo, U.S.A.), 300 MHz ^{1}H NMR spectrophotometer (Bruker, Switzerland) were used and for pH measurements, an Elico pH meter model LI120 were used.

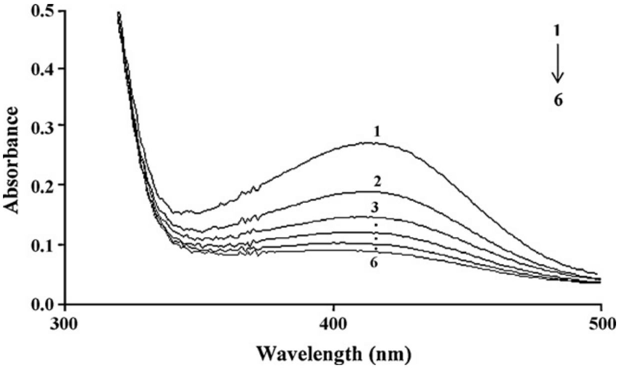


Fig. 1. UV–vis spectral changes during the oxidation of DL-ornithine by alkaline diperiodatocuprate(III) at 298 K, [DPC] = 5.0 × 10^{-5}, [OMH] = 5.0 × 10^{-4}, [OH$^-$] = 0.08 and I = 0.20 mol dm^{-3} with scanning time of (1) 1.0 min, (2) 2.0 min, (3) 3.0 min, (4) 4.0 min, (5) 5.0 min and (6) 6.0 min.

2.3. Kinetic measurements

Since the initial rate was too fast to be monitored by usual methods in the catalyzed reaction, the kinetic measurements were performed on a Hitachi 150-20 UV-visible spectrophotometer attached to a rapid kinetic accessory (HI-TECH SFA-12). The oxidation of OMH by DPC was followed under pseudo-first-order conditions where [OMH] > [DPC] in both uncatalyzed and catalyzed reactions at 25.0 ± 0.1 °C, unless otherwise specified. In the absence of catalyst, the reaction was initiated by mixing DPC with the OMH solution which also contained required concentrations of KNO_3, KOH, and KIO_4. The reaction in the presence of catalyst Ru(III) was initiated by mixing DPC with the OMH solution which also contained the required concentration of KNO_3, KOH, KIO_4, and Ru(III) catalyst. The progress of the reaction was monitored spectrophotometrically at 415 nm (i.e., decrease in absorbance due to DPC with the molar absorbency index, 'ε' to be 6231 ± 100 dm^3 mol^{-1} cm^{-1} (literature ε = 6230 [23]) in both catalyzed and uncatalyzed reaction), which is the maximum absorption wavelength of DPC. The spectral changes during the chemical reaction for the standard condition at 298 K are shown in Fig. 1. It is evident from the figure that the concentration of DPC decreases at 415 nm. It was verified that there was almost no interference from other species in the reaction mixture at this wavelength.

During the kinetics, a constant concentration *viz.* 1.0 × 10^{-5} mol dm^{-3} of KIO_4 was used throughout the study unless otherwise stated. Since excess of periodate is present in DPC, the possibility of oxidation of OMH by periodate in alkaline medium at 25 °C was tested and found that there was no significant interference due to KIO_4 under experimental conditions. The total concentrations of periodate and OH$^-$ was calculated by considering the amount present in DPC solution and that additionally added. Kinetic runs were also carried out in N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of the 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. The added carbonate had no effect on the reaction rates.

The orders for various species were determined from the slopes of plots of log(k_U or k_C) *vs.* respective concentration of species except for [DPC] in which non-variation of 'k_U or k_C' was observed as expected to the reaction condition. The rate constants were reproducible to within ±5%. Regression analysis of experimental data to obtain regression coefficient r and the standard deviation S, of points from the regression line, was performed with the Microsoft office Excel 2003 program.

3. Results

3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPC to OMH in presence of constant amount of OH$^-$, KIO_4, and

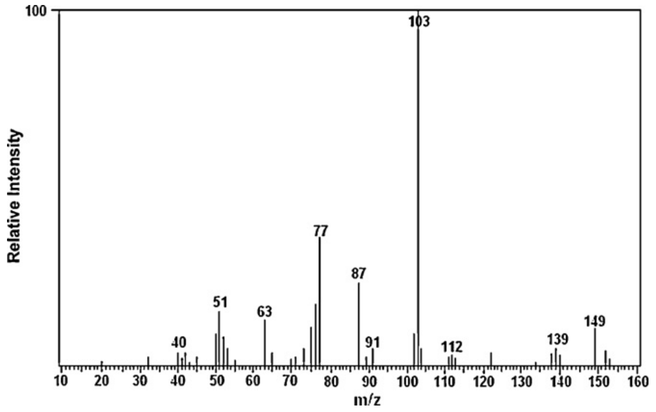
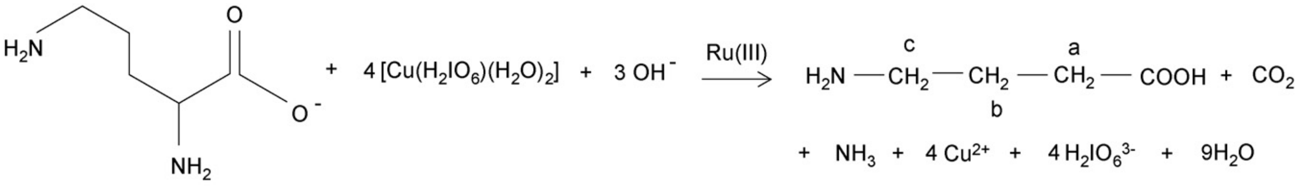


Fig. 2. Mass spectrum of reaction product, 4-aminobutyric acid with its molecular ion peak at 103 *m*/*z*.

KNO_3 in uncatalyzed reaction and a constant amount of Ru(III) in catalyzed reaction were kept for 6 h in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was assayed by measuring the absorbance at 415 nm. The results indicated 1:4 stoichiometry for both the reactions as given in Eq. (1):



(1)

After completion of reaction, the reaction mixture was acidified, concentrated and extracted with ether. The reaction product was further recrystallized from aqueous alcohol. The main reaction product was identified as 4-aminobutyric acid. This was the only organic product obtained in the oxidation which was confirmed by a single spot on thin layer chromatography and was characterized by FT-IR, GC–MS and ^1H NMR spectral studies.

The IR spectroscopy showed a >C=O stretching of carboxylic acid at 1708 cm^{-1} indicating the presence of acidic C=O group, O–H stretching of carboxylic acid at 2848 cm^{-1} indicating the presence of acidic –OH group, and also N–H stretching at 3427 cm^{-1} indicating the presence of $-NH_2$ group in 4-aminobutyric acid. GC–MS data was obtained on a QP-2010S Shimadzu gas chromatograph mass spectrometer. The mass spectral data showed a molecular ion peak at 103 *m*/*z* confirming the presence of 4-aminobutyric acid (Fig. 2). All other peaks observed in GC–MS can be interpreted in accordance with the observed structure of 4-aminobutyric acid. It was also subjected to ^1H NMR spectrum ($CDCl_3$), two triplet at 2.31 δ (a) and 2.69 δ (c) and a multiplet at 1.84 δ (due to (b) CH_2), 5.44 δ (s, 2H due to $-NH_2$) and 11.6 δ (s, H due to –COOH). $-NH_2$ and –OH disappeared on D_2O exchange.

The by-products were identified as ammonia by Nessler's reagent [21] and CO_2 was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through the tube containing limewater. Finally copper(II) was identified by UV–vis spectra.

3.2. Reaction orders

As the diperiodatocuprate(III) oxidation of DL-ornithine in alkaline medium proceeds with a measurable rate in the absence of Ru(III), the catalyzed reaction is understood to occur in parallel paths with contributions from both the catalyzed and uncatalyzed paths. Thus the total rate constant (k_T) is equal to the sum of the rate constants of the catalyzed (k_C) and uncatalyzed (k_U) reactions, so $k_C = k_T - k_U$. Hence the reaction orders have been determined from the slopes of log k_C *vs.* log(concentration) plots by varying the concentrations of OMH, IO_4^-, OH^-, and catalyst Ru(III), in turn while keeping others constant.

3.3. Evaluation of pseudo-first-order rate constants

The oxidant [DPC] was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} at fixed [OMH], [KOH], and [KIO_4] in both the cases of uncatalyzed and catalyzed reactions. The pseudo-first-order rate constants (k_U or k_C), in both the cases were determined from the log(absorbance) *vs.* time plots. The plots were linear up to 85% completion of reaction under the range of [OH^-] used ($r \geq 0.9549$, $S \leq 0.016$). The fairly constant pseudo-first-order rate constants, k_U and k_C, indicate that the order with respect to [DPC] was unity (Table 1 uncatalyzed) (Table 2 Ru(III) catalyzed).

3.4. Effect of varying [DL-ornithine]

The effect of OMH was studied for both the cases in the range of 6.0×10^{-5} to 6.0×10^{-4} mol dm^{-3} at constant concentrations of DPC, OH^-, IO_4^- and a constant ionic strength of 0.20 mol dm^{-3} in uncatalyzed and with constant concentration of Ru(III) in catalyzed reaction. In the case of uncatalyzed reaction as well as catalyzed reaction, at constant temperature, the k_U and k_C values increased with increase in [OMH]. The order with respect to [OMH] was less than unity (Table 1 uncatalyzed) (Table 2 Ru(III) catalyzed) ($r \geq 0.9984$, $S \leq 0.009$). This was also confirmed by the plots of k_U *vs.* $[OMH]^{0.56}$ and k_C *vs.* $[OMH]^{0.61}$ which were linear rather than the direct plot of k_U *vs.* [OMH] and k_C *vs.* [OMH] (Fig. 3).

3.5. Effect of varying [alkali]

The effect of alkali was studied for both the cases in the range of 0.02–0.20 mol dm^{-3} at constant concentrations of DPC, OMH, IO_4^- and ionic strength in uncatalyzed and with constant concentration of Ru(III) in catalyzed reaction. The rate constants increased with increase in [alkali] and the order was found to be less than unity i.e., 0.41 in uncatalyzed and 0.39 in Ru(III) catalyzed reaction. (Table 1 uncatalyzed) (Table 2 Ru(III) catalyzed) ($r \geq 0.9942$, $S \leq 0.007$).

3.6. Effect of varying [periodate]

The effect of periodate was studied for both the cases in the range of 5.0×10^{-6} to 5.0×10^{-5} mol dm^{-3} at constant concentrations of DPC, OMH, OH^- and ionic strength in uncatalyzed and with constant concentration of Ru(III) in catalyzed reaction. The experimental results indicated that the k_U and k_C values decreased with increase in [IO_4^-]. The order with respect to IO_4^- was negative fractional i.e., −0.45 in uncatalyzed and −0.44 in Ru(III) catalyzed reaction. (Table 1 uncatalyzed) (Table 2 Ru(III) catalyzed) ($r \geq 0.9968$, $S \leq 0.004$).

3.7. Effect of varying [Ru(III)]

The [Ru(III)] concentrations were varied from 2.0×10^{-7} to 2.0×10^{-6} mol dm^{-3} range, at constant concentration of DPC, OMH,

Table 1

Effect of variation of [DPC], [OMH], $[OH^-]$ and $[IO_4^-]$ on the oxidation of DL-ornithine by diperiodatocuprate(III) in aqueous alkaline medium at 298 K and $I = 0.20\ mol\ dm^{-3}$.

[DPC] ($\times 10^5\ mol\ dm^{-3}$)	[OMH] ($\times 10^4\ mol\ dm^{-3}$)	$[OH^-]$ ($\times 10^1\ mol\ dm^{-3}$)	$[IO_4^-]$ ($\times 10^5\ mol\ dm^{-3}$)	k_U ($\times 10^3\ s^{-1}$)	
				Found	Calculated
1.0	5.0	0.8	1.0	2.90	2.96
3.0	5.0	0.8	1.0	3.00	2.96
5.0	5.0	0.8	1.0	2.88	2.96
8.0	5.0	0.8	1.0	2.53	2.96
10.0	5.0	0.8	1.0	2.30	2.96
5.0	0.6	0.8	1.0	0.85	0.80
5.0	1.0	0.8	1.0	1.28	1.20
5.0	2.0	0.8	1.0	2.08	1.96
5.0	5.0	0.8	1.0	2.88	2.96
5.0	6.0	0.8	1.0	3.38	3.16
5.0	5.0	0.2	1.0	1.48	1.47
5.0	5.0	0.4	1.0	2.15	2.22
5.0	5.0	0.8	1.0	2.88	2.96
5.0	5.0	1.0	1.0	3.36	3.20
5.0	5.0	2.0	1.0	3.74	3.72
5.0	5.0	0.8	0.5	3.80	3.60
5.0	5.0	0.8	0.8	3.30	3.18
5.0	5.0	0.8	1.0	2.88	2.96
5.0	5.0	0.8	3.0	1.85	1.75
5.0	5.0	0.8	5.0	1.33	1.26

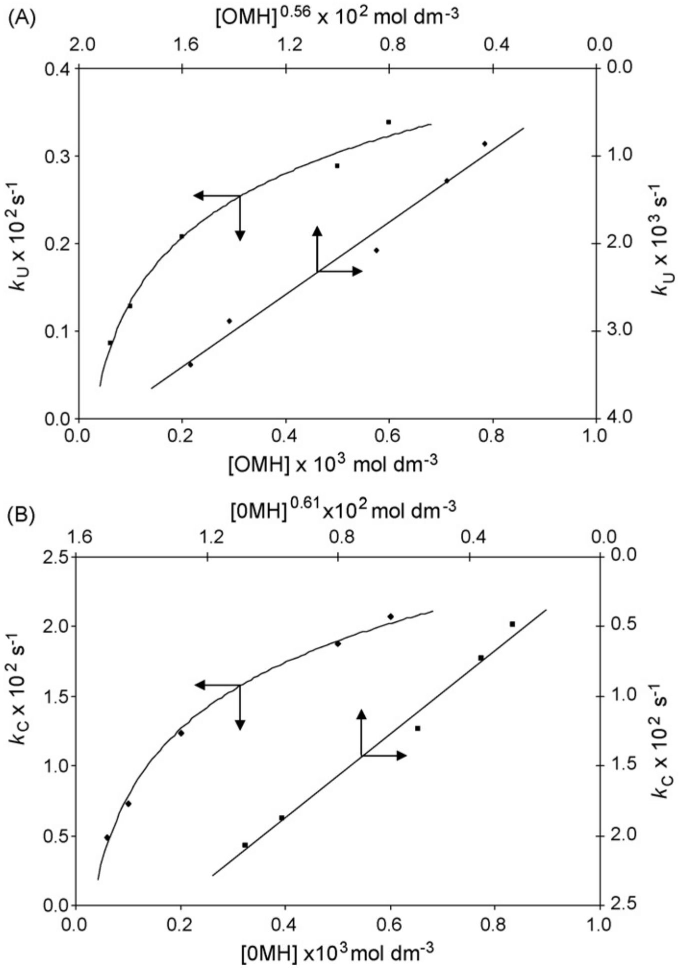


Fig. 3. Plots of (A) k_U *vs.* $[OMH]^{0.56}$ and k_U *vs.* [OMH] (conditions as in Table 1) and (B) k_C *vs.* $[OMH]^{0.61}$ and k_C *vs.* [OMH] (conditions as in Table 2).

and alkali and constant ionic strength. The order in [Ru(III)] was found to be unity from the linearity of the plot of k_C *vs.* [Ru(III)] (Table 2 Ru(III) catalyzed) (Fig. 4).

3.8. *Effect of varying ionic strength (I) and dielectric constant (D)*

The effect of ionic strength (*I*) was studied by varying $[KNO_3]$. The dielectric constant of the medium (*D*) was studied by varying the t-butyl alcohol and water percentage. It was found that there was no significant effect of ionic strength and dielectric constant of the medium on the rate of reaction in both the cases of uncatalyzed and catalyzed reactions.

3.9. *Effect of initially added products*

Initially added products, copper(II) ($CuSO_4$) and 4-aminobutyric acid did not have any significant effect on the rate of reaction (for both the cases).

Thus, from the observed experimental results:

The rate law for uncatalyzed reaction is given as follows:

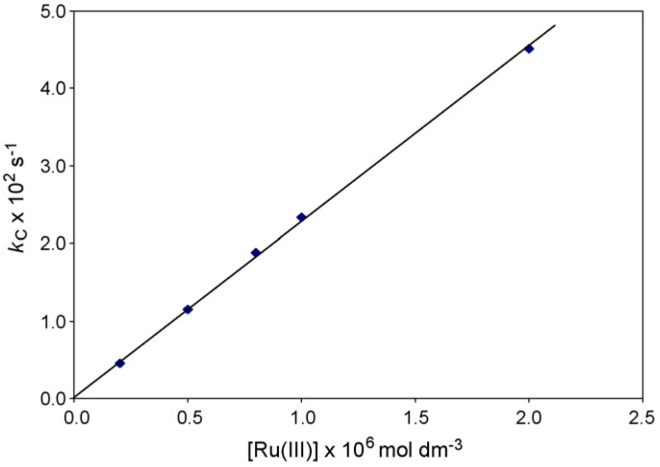


Fig. 4. Unit order plot of [Ru(III)] *vs.* k_C.

Table 2
Effect of variation of [DPC], [OMH], [OH$^-$], [IO$_4^-$] and [Ru(III)] on the ruthenium(III) catalyzed oxidation of DL-ornithine by diperiodatocuprate(III) in aqueous alkaline medium at 298 K and I = 0.20 mol dm^{-3}.

[DPC] ($\times 10^5$ mol dm^{-3})	[OMH] ($\times 10^4$ mol dm^{-3})	[OH$^-$] ($\times 10^1$ mol dm^{-3})	[IO$_4^-$] ($\times 10^5$ mol dm^{-3})	[Ru(III)] ($\times 10^7$ mol dm^{-3})	k_T ($\times 10^2$ s^{-1})	k_U ($\times 10^3$ s^{-1})	k_C ($\times 10^2$ s^{-1})	
							Found	Calculated
1.0	5.0	0.8	1.0	8.0	2.05	2.90	1.76	1.84
3.0	5.0	0.8	1.0	8.0	2.13	3.00	1.83	1.84
5.0	5.0	0.8	1.0	8.0	2.16	2.88	1.87	1.84
8.0	5.0	0.8	1.0	8.0	2.01	2.53	1.75	1.84
10.0	5.0	0.8	1.0	8.0	2.01	2.30	1.78	1.84
5.0	0.6	0.8	1.0	8.0	0.57	0.85	0.49	0.46
5.0	1.0	0.8	1.0	8.0	0.86	1.28	0.73	0.69
5.0	2.0	0.8	1.0	8.0	1.44	2.08	1.23	1.14
5.0	5.0	0.8	1.0	8.0	2.16	2.88	1.87	1.84
5.0	6.0	0.8	1.0	8.0	2.40	3.38	2.06	2.00
5.0	5.0	0.2	1.0	8.0	1.10	1.48	0.95	0.94
5.0	5.0	0.4	1.0	8.0	1.56	2.15	1.35	1.39
5.0	5.0	0.8	1.0	8.0	2.16	2.88	1.87	1.84
5.0	5.0	1.0	1.0	8.0	2.40	3.36	2.07	1.98
5.0	5.0	2.0	1.0	8.0	2.67	3.74	2.29	2.29
5.0	5.0	0.8	0.5	8.0	2.70	3.80	2.32	2.21
5.0	5.0	0.8	0.8	8.0	2.40	3.30	2.07	1.98
5.0	5.0	0.8	1.0	8.0	2.16	2.88	1.87	1.84
5.0	5.0	0.8	3.0	8.0	1.32	1.85	1.14	1.11
5.0	5.0	0.8	5.0	8.0	0.99	1.33	0.85	0.80
5.0	5.0	0.8	1.0	2.0	0.74	2.88	0.45	0.46
5.0	5.0	0.8	1.0	5.0	1.43	2.88	1.14	1.15
5.0	5.0	0.8	1.0	8.0	2.16	2.88	1.87	1.84
5.0	5.0	0.8	1.0	10.0	2.61	2.88	2.33	2.31
5.0	5.0	0.8	1.0	20.0	4.80	2.88	4.51	4.62

$$\text{Rate} = k_U[\text{DPC}]^{1.0}[\text{OMH}]^{0.56}[\text{OH}^-]^{0.41}[\text{IO}_4{}^-]^{-0.45}$$

The rate law for Ru(III) catalyzed reaction is given as follows:

$$\text{Rate} = k_C[\text{DPC}]^{1.0}[\text{OMH}]^{0.61}[\text{OH}^-]^{0.39}[\text{Ru(III)}]^{1.0}[\text{IO}_4{}^-]^{-0.44}$$

3.10. Polymerization study

For both uncatalyzed and catalyzed reactions the possibility of free radicals was detected as follows. The reaction mixture, to which a known quantity of acrylonitrile (scavenger) had been added initially, 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 reactions. The blank experiments of either DPC or DL-ornithine alone with acrylonitrile did not induce any polymerization under the same condition as those induced for the reaction mixture. Initially added acrylonitrile decreases the rate of reaction indicating free radical intervention, which is the case in earlier work [24].

3.11. Effect of temperature (T)

The kinetics was studied at four different temperatures 288, 298, 308 and 318 K under varying concentrations of DL-ornithine, alkali and periodate, keeping other conditions constant for uncatalyzed reaction. The rate constants (k_1), of the slow step of Scheme 1 were obtained from the slopes and the intercepts of the plots of $1/k_U$ *vs.* 1/[OMH] at four different temperatures. The values are given in Table 3. The energy of activation for the rate determining step was obtained by the least-squares method of plot of log k_1 *vs.* $1/T$ and other activation parameters calculated are presented in Table 3.

For catalyzed reaction the influence of temperature on the rate of reaction was studied at 288, 298, 308 and 318 K. The rate constants (k_2), of the slow step of Scheme 2 were obtained from the slopes and the intercepts of the plots of [Ru(III)]/k_C *vs.* 1/[OMH] at four different temperatures. The values are given in Table 4. The energy of activation for the rate determining step was obtained by the least-squares method of plot of log k_2 *vs.* $1/T$ and other activation parameters calculated for the reaction are presented in Table 4.

3.12. Catalytic activity

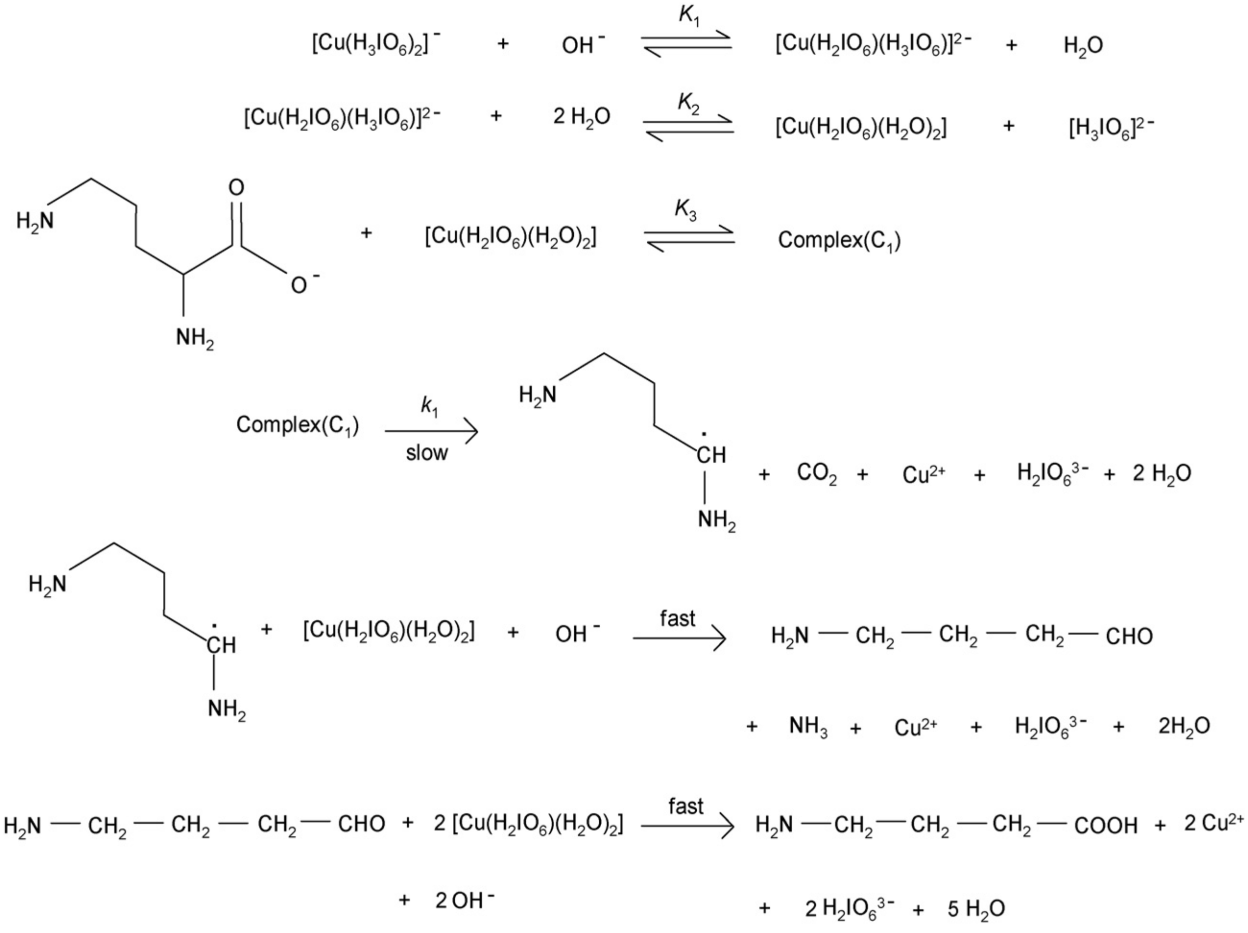
It has been pointed out by Moelwyn-Hughes [25] that in the presence of catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously, so that:

$$k_T = k_U + K_C[\text{Ru(III)}]^x \qquad (2)$$

Here k_T is the observed pseudo-first-order rate constant in the presence of Ru(III) catalyst; k_U, the pseudo-first-order rate constant for uncatalyzed; K_C, the catalytic constant and 'x' the order of the reaction with respect to Ru(III). In the present investigations; x values for the standard run were found to be unity.

Then, the value of K_C is calculated using the equation:

$$K_C = \frac{k_T - k_U}{[\text{Ru(III)}]^x} = \frac{k_C}{[\text{Ru(III)}]} \quad (\text{where}, \quad k_T - k_U = k_C) \qquad (3)$$

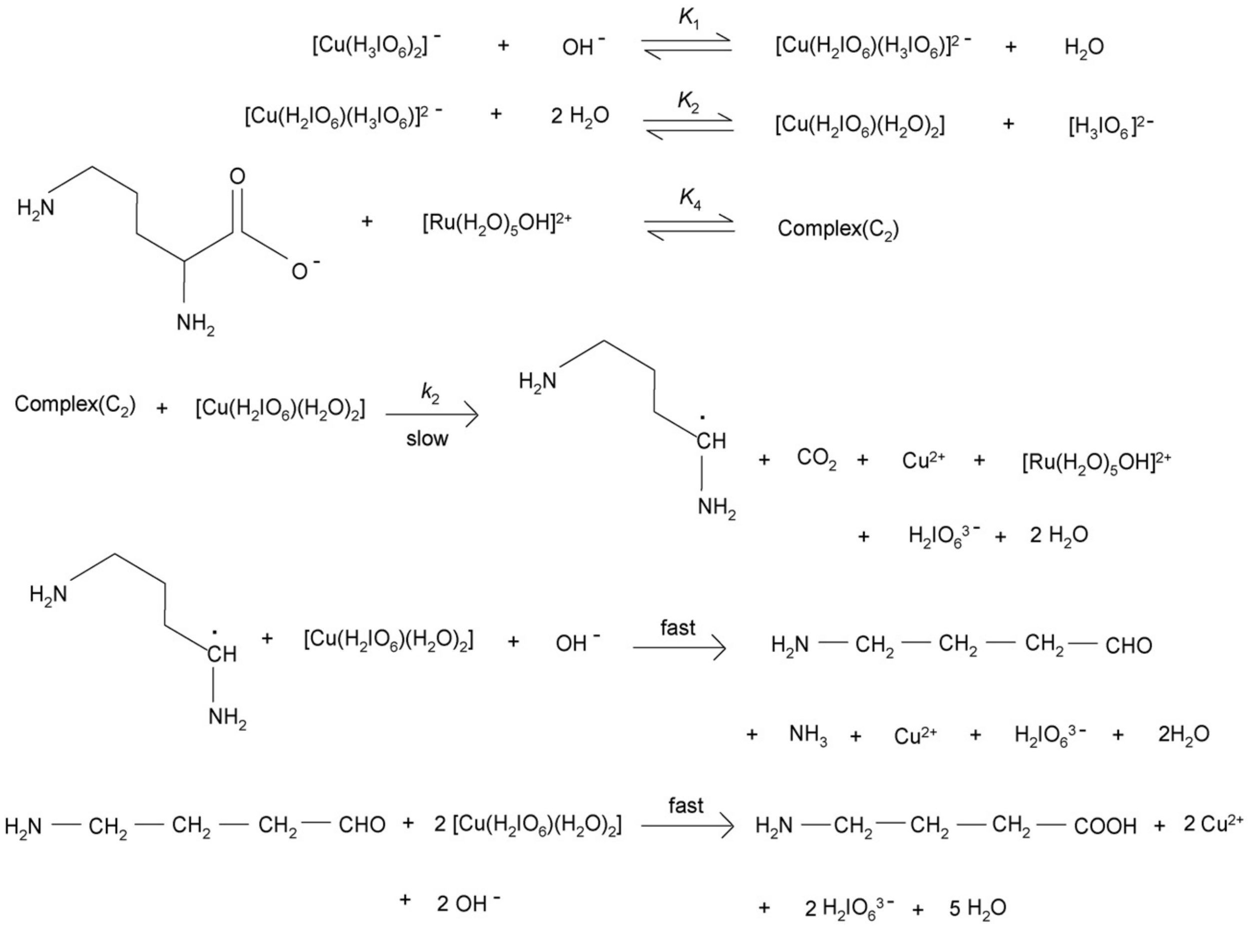


Scheme 1. Detailed scheme for the oxidation of DL-ornithine by alkaline diperidatocuprate(III).

Table 3
Activation parameters and thermodynamic quantities for the oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium with respect to the slow step of Scheme1: (A) effect of temperature, (B) activation parameters (Scheme 1), (C) effect of temperature on K_1, K_2 and K_3 for the oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium and (D) thermodynamic quantities using K_1, K_2 and K_3.

Temperature (K)	k_1 ($\times 10^2$ s^{-1})		
(A)			
288	0.23		
298	0.47		
308	0.95		
318	1.90		
Parameters	**Values**		
(B)			
E_a (kJ mol^{-1})	52.7 ± 2.0		
$\Delta H^\#$ (kJ mol^{-1})	50.2 ± 2.0		
$\Delta S^\#$ (J K^{-1} mol^{-1})	−121 ± 5		
$\Delta G^\#$ (kJ mol^{-1})	86 ± 4		
log A	6.9 ± 0.2		
Temperature (K)	**K_1 ($\times 10^1$ dm^3 mol^{-1})**	**K_2 ($\times 10^4$ mol dm^{-3})**	**K_3 ($\times 10^{-4}$ dm^3 mol^{-1})**
(C)			
288	0.87	1.25	4.70
298	1.24	1.01	3.66
308	2.22	0.85	2.48
318	4.33	0.69	1.68
Thermodynamic quantities	**Values from K_1**	**Values from K_2**	**Values from K_3**
(D)			
ΔH (kJ mol^{-1})	40.6	−14.7	−26.3
ΔS (J K^{-1} mol^{-1})	120	−126	−1.68
ΔG_{298} (kJ mol^{-1})	5.15	22.8	−26.0

[DPC] = 5.0×10^{-5}, [OMH] = 5.0×10^{-4}, [OH$^-$] = 0.08, [IO$_4^-$] = 1.0×10^{-5} and I = 0.20/mol dm^{-3}.



Scheme 2. Detailed scheme for Ru(III) catalyzed oxidation of DL-ornithine by alkaline diperidatocuprate(III).

Table 4
Activation parameters and thermodynamic quantities for the ruthenium(III) catalyzed oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium with respect to the slow step of Scheme 2: (A) effect of temperature, (B) activation parameters (Scheme 2), (C) effect of temperature on K_1, K_2 and K_4 for the ruthenium(III) catalyzed oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium and (D) thermodynamic quantities using K_1, K_2 and K_4.

Temperature (K)	k_2 ($\times 10^{-5}$ dm^3 mol^{-1} s^{-1})
(A)	
288	0.22
298	0.40
308	0.73
318	1.35

Parameters	Values
(B)	
E_a (kJ mol^{-1})	46 ± 2
$\Delta H^{\#}$ (kJ mol^{-1})	43.4 ± 0.5
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	-11.5 ± 1.0
$\Delta G^{\#}$ (kJ mol^{-1})	47 ± 5
log A	12.6 ± 0.2

Temperature (K)	K_1 ($\times 10^{1}$ dm^3 mol^{-1})	K_2 ($\times 10^{4}$ mol dm^{-3})	K_4 ($\times 10^{-4}$ dm^3 mol^{-1})
(C)			
288	0.60	7.23	0.76
298	1.35	2.54	1.29
308	2.60	0.94	2.02
318	5.98	0.36	2.82

Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_4
(D)			
ΔH (kJ mol^{-1})	54.4	−75.8	33.3
ΔS (J K^{-1} mol^{-1})	166	−323	190
ΔG_{298} (kJ mol^{-1})	4.95	20.5	−23.4

$[\mathrm{DPC}] = 5.0 \times 10^{-5}$, $[\mathrm{OMH}] = 5.0 \times 10^{-4}$, $[\mathrm{OH^-}] = 0.08$, $[\mathrm{Ru(III)}] = 8.0 \times 10^{-7}$, $[\mathrm{IO_4^-}] = 1.0 \times 10^{-5}$ and $I = 0.20$/mol dm^{-3}.

Table 5
Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values.

	K_C ($\times 10^{-4}$)
Temperature (K)	
288	1.17
298	2.34
308	4.68
318	9.36
E_a (kJ mol^{-1})	52
$\Delta H^{\#}$ (kJ mol^{-1})	50.3
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−110
$\Delta G^{\#}$ (kJ mol^{-1})	83
log A	7.5

$[\mathrm{DPC}] = 5.0 \times 10^{-5}$, $[\mathrm{OMH}] = 5.0 \times 10^{-4}$, $[\mathrm{OH^-}] = 0.08$, $[\mathrm{Ru(III)}] = 8.0 \times 10^{-7}$, $[\mathrm{IO_4^-}] = 1.0 \times 10^{-5}$ and $I = 0.20$/mol dm^{-3}.

The values of K_C were evaluated for Ru(III) catalyst at different temperatures and were found to vary at different temperatures. Further, plots of log K_C *vs.* $1/T$ were linear and the values of energy of activation and other activation parameters with reference to catalyst were computed. These results are summarized in Table 5. The value of K_C is 2.34×10^4 at 298 K.

4. Discussion

The water-soluble copper(III) periodate complex is reported [26] to be $[\mathrm{Cu(HIO_6)_2(OH)_2}]^{7-}$. However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as $\mathrm{HIO_6}^{4-}$ (as present in the complex) as is evident from its involvement in the multiple equilibria [27] (4)–(6) depending on the pH of the solution:

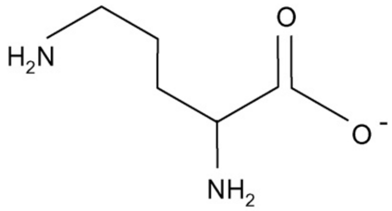
$$\mathrm{H_5IO_6} \rightleftharpoons \mathrm{H_4IO_6}^- + \mathrm{H}^+ \quad (4)$$

$$\mathrm{H_4IO_6}^- \rightleftharpoons \mathrm{H_3IO_6}^{2-} + \mathrm{H}^+ \quad (5)$$

$$\mathrm{H_3IO_6}^{2-} \rightleftharpoons \mathrm{H_2IO_6}^{3-} + \mathrm{H}^+ \quad (6)$$

Periodic acid exists as $\mathrm{H_5IO^-}_6$ in an acid medium and as $\mathrm{H_4IO^-}_6$ around pH 7. Thus, under the conditions employed in alkaline medium, the main species are expected to be $\mathrm{H_3IO_6}^{2-}$ and $\mathrm{H_2IO_6}^{3-}$. At higher concentrations, periodate also tends to dimerize. 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), $[\mathrm{Cu(H_2IO_6)(H_3IO_6)}]^{2-}$, a conclusion also supported by earlier work [28,29].

It is known that DL-ornithine exists in the form of Zwitterion [30] in aqueous medium. In highly acidic medium it exists in the protonated form, where as in highly basic medium it is in the deprotonated form [30].



4.1. Mechanism for uncatalyzed reaction

The reaction between DPC and OMH in alkaline medium presents [DPC]/[OMH] = 1:4 stoichiometry. Since the reaction was enhanced by [OH$^-$], added periodate retarded the rate and first order dependency in [DPC] and fractional order in [OMH] and [OH$^-$], a plausible reaction mechanism has been proposed which also explains all other experimental observations as shown in Scheme 1.

Lister [31] proposed the copper(III) periodate in alkaline medium into three forms as diperiodatocuprate(III) (DPC),

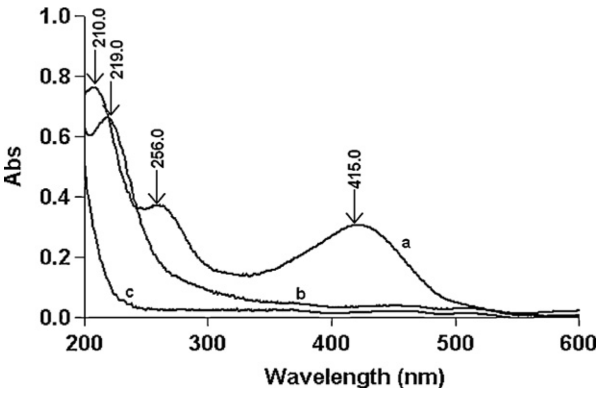


Fig. 5. Spectroscopic evidence for the complex formation between DPC and OMH (a) UV–vis spectra of DPC complex (415, 258 and 210 nm), (b) UV–vis spectra of mixture of DPC and OMH and (c) UV–vis spectra of OMH.

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, in view of the negative less than unit order in periodate on rate of reaction, monoperiodatocuprate(III) MPC is considered to be the active species of copper(III) periodate complex. 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. (7) and (8):

$$[\mathrm{Cu(H_3IO_6)_2}]^- + \mathrm{OH^-} \rightleftharpoons [\mathrm{Cu(H_2IO_6)(H_3IO_6)}]^{2-} + \mathrm{H_2O} \qquad (7)$$

$$[\mathrm{Cu(H_2IO_6)(H_3IO_6)}]^{2-} + 2\mathrm{H_2O} \rightleftharpoons [\mathrm{Cu(H_2IO_6)(H_2O)_2}] + [\mathrm{H_3IO_6}]^{2-} \qquad (8)$$

The inverse fractional order in $[\mathrm{IO_4}^-]$ might also be due to this reason. The less than unit order in [OMH] presumably results from formation of a complex (C_1) between the oxidant and DL-ornithine prior to the formation of the products. K_3 is the composite equilibrium constant comprising the equilibrium to bind OMH to MPC species to form a complex (C_1). Then this complex (C_1) decomposes in a slow step to form a free radical derived from DL-ornithine. This free radical species further reacts with another molecule of MPC species in a fast step to form 4-aminobutaraldehyde intermediate. This 4-aminobutaraldehyde then reacts with two more moles of MPC in a further fast step to form products such as 4-aminobutyric acid, Cu(II) and periodate. All these results may be interpreted in the form of Scheme 1.

Since Scheme 1 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 infra). 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 DPC (5.0×10^{-5}), OMH ((5.0×10^{-4}), $[\mathrm{OH^-}] = 0.08\ \mathrm{mol\,dm^{-3}}$) and a mixture of both. A bathochromic shift of about 9 nm from 210 to 219 nm in the spectra of DPC to mixture of DPC and OMH was observed (Fig. 5). The Michaelis–Menten plot proved the complex formation between oxidant and substrate, which explains less than unit order in [OMH]. Such a complex between an oxidant and substrate has also been observed in other studies [34,35].

From Scheme 1, the rate law (10) can be derived:

$$\mathrm{Rate} = -\frac{d[\mathrm{DPC}]}{dt} = \frac{k_1K_1K_2K_3[\mathrm{DPC}][\mathrm{OMH}][\mathrm{OH^-}]}{[\mathrm{H_3IO_6}^{2-}] + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6}^{2-}] + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3[\mathrm{OH^-}][\mathrm{OMH}]} \qquad (9)$$

$$k_\mathrm{U} = \frac{\mathrm{Rate}}{[\mathrm{DPC}]} = \frac{k_1K_1K_2K_3[\mathrm{OMH}][\mathrm{OH^-}]}{[\mathrm{H_3IO_6}]^{2-} + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6}]^{2-} + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3[\mathrm{OH^-}][\mathrm{OMH}]} \qquad (10)$$

which explains all the observed kinetic orders of different species.

The rate law (10) can be rearranged into the following form which is suitable for verification:

$$\frac{1}{k_\mathrm{U}} = \frac{[\mathrm{H_3IO_6}^{2-}]}{k_1K_1K_2K_3[\mathrm{OH^-}][\mathrm{OMH}]} + \frac{[\mathrm{H_3IO_6}^{2-}]}{k_1K_2K_3[\mathrm{OMH}]} + \frac{1}{k_1K_3[\mathrm{OMH}]} + \frac{1}{k_1} \qquad (11)$$

According to Eq. (10), other conditions being constant, plots of $1/k_\mathrm{U}$ *vs.* 1/[OMH], $1/k_\mathrm{U}$ *vs.* $1/[\mathrm{OH^-}]$ and $1/k_\mathrm{U}$ *vs.* $[\mathrm{H_3IO_6}^{2-}]$ should be linear and are found to be so (Fig. 6). The slopes and intercepts of such plots lead to the values of K_1, K_2, K_3 and k_1 (Table 3). The values of K_1 and K_2 are in good agreement with the literature [36]. Using these constants, the rate constants were calculated over different experimental conditions, and there is a reasonable agreement between the calculated and the experimental values (Table 1), which fortifies the proposed mechanism (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 compared to the dissociation of hydrolyzed species in alkaline medium.

The negligible 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 different equilibrium steps, in Scheme 1 can be evaluated as follows. The [OMH], $[\mathrm{OH^-}]$, and $[\mathrm{H_3IO_6}^{2-}]$ (Table 1) were varied at four different temperatures. The plots of $1/k_\mathrm{U}$ *vs.* 1/[OMH], $1/k_\mathrm{U}$ *vs.* $1/[\mathrm{OH^-}]$ and $1/k_\mathrm{U}$ *vs.* $[\mathrm{H_3IO_6}^{2-}]$ should be linear and are found to be so. From the slopes and intercepts, the values of K_1, K_2 and K_3 were calculated at different temperatures. A vant Hoff's plot was made for the variation of K_1, K_2 and K_3 with temperature ($\log K_1$ *vs.* $1/T$, $\log K_2$ *vs.* $1/T$ and $\log K_3$ *vs.* $1/T$). The values of enthalpy of reaction ΔH, entropy of reaction ΔS 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 ΔH value ($40.6\ \mathrm{kJ\,mol^{-1}}$) from K_1 with that of $\Delta H^\#$ ($50.2\ \mathrm{kJ\,mol^{-1}}$) of rate-limiting step supports that the reaction before the rate determining step is fairly fast as it involves low activation energy [37,38]. A high negative value of $\Delta S^\#$ ($-121\ \mathrm{J\,K^{-1}\,mol^{-1}}$) suggests that intermediate complex (C_1) is more ordered than the reactants [39].

4.2. Mechanism for Ru(III) catalyzed reaction

Ru(III) chloride acts as an efficient catalyst in many redox reactions, particularly in an alkaline medium [24,40]. In the present study it is quite probable that the $[\mathrm{Ru(H_2O)_5OH}]^{2+}$ species might assume the general form $[\mathrm{Ru(III)(OH)}_x]^{3-x}$. The x value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The remainder of the coordination sphere would be filled by water molecules. Hence, under the conditions employed, e.g., $[\mathrm{OH^-}] \gg [\mathrm{Ru(III)}]$, ruthenium(III) is mostly present as the hydroxylated species, $[\mathrm{Ru(H_2O)_5OH}]^{2+}$ [41].

In the earlier reports of Ru(III) catalyzed oxidation, it was observed that [42], if there exists a fractional order dependence

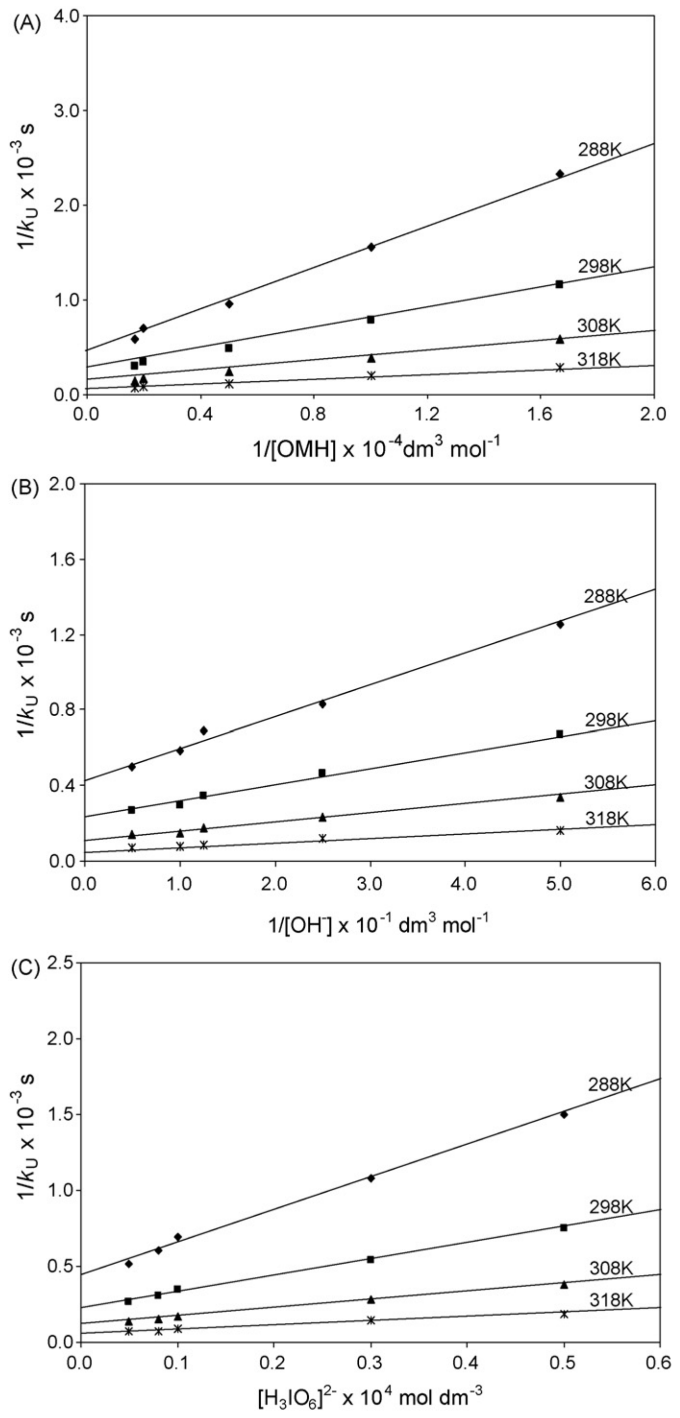


Fig. 6. Verification of rate law (10) for the oxidation of DL-ornithine by diperiodatocuprate(III). Plots of (A) $1/k_U$ *vs.* $1/[\mathrm{OMH}]$, (B) $1/k_U$ *vs.* $1/[\mathrm{OH}^-]$ and (C) $1/k_U$ *vs.* $[\mathrm{H_3IO_6}]^{2-}$, at four different temperatures (conditions as in Table 1).

with respect to [substrate] and [Ru(III)], and unit order with respect to [oxidant], it leads to the formation of Ru(III)–substrate complex. This complex is further oxidized by the oxidant to Ru(IV)–substrate complex followed by the rapid redox decomposition with regeneration of Ru(III) catalyst. In case [43], if the process involves a zeroth order dependence with respect to [oxidant], first order with respect to [Ru(III)] and a fractional order with respect to [substrate], it leads to the formation of Ru(III)–substrate complex and further cleaves to Ru(I) species which is rapidly oxidized by the oxidant to regenerate Ru(III) catalyst.

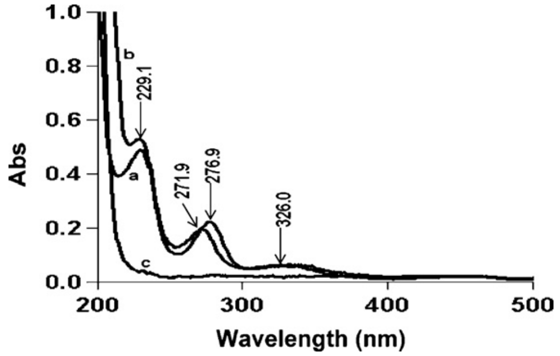


Fig. 7. Spectroscopic evidence for the complex formation between Ru(III) and OMH (a) UV–vis spectra of Ru(III) (229.1, 276.9 and 326 nm) and (b) UV–vis spectra of mixture of Ru(III) and OMH (229.1, 271.9, 326 nm) and (c) UV–vis spectra of OMH.

In the present investigation, the reaction was enhanced by $[\mathrm{OH}^-]$, added periodate retarded the rate, first order dependency in [DPC] and catalyst [Ru(III)] and fractional order in [OMH] and $[\mathrm{OH}^-]$ was observed. To explain the observed orders the following Scheme 2 has been proposed for ruthenium(III) catalyzed reaction considering its OMH as anionic form of OMH in alkaline medium.

In this study, in view of the negative less than unit order of periodate on the rate of reaction, monoperiodatocuprate(III) MPC is considered to be the active species of copper(III) periodate complex. 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 already shown in Eqs. (7) and (8). Anionic species of OMH reacts with ruthenium(III) active species to form a complex (C_2) which further reacts with one mole of MPC in a slow step to give the free radical species of OMH, Cu(II) with regeneration of catalyst, ruthenium(III). Further this free radical species of OMH reacts with one more molecule of MPC species in a fast step to form 4-aminobutaraldehyde intermediate. This 4-aminobutaraldehyde then reacts with two more moles of MPC in a further fast step to form products such as 4-aminobutyric acid, Cu(II) and periodate. All these results may be interpreted in the form of Scheme 2. Similar type of key step, in the mechanism, has been proposed for the catalyzed reaction in the earlier studies [36].

Spectroscopic evidence for the complex formation between Ru(III) and OMH was obtained from UV–vis spectra of OMH (5.0×10^{-4}), Ru(III) (8.0×10^{-7}, $[\mathrm{OH}^-]=0.08\,\mathrm{mol\,dm^{-3}}$) and a mixture of both. A hypsochromic shift of about 5 nm from 276.9 to 271.9 nm in the spectra of Ru(III) to the mixture of Ru(III) and OMH was observed (Fig. 7). The Michaelis-Menten plot proved the complex formation between catalyst and substrate, which explains less than unit order in [OMH]. Such a complex between a catalyst and substrate has also been observed in other studies [44].

From Scheme 2, the rate law (13) can be derived:

$$\mathrm{Rate}=\frac{-\mathrm{d[DPC]}}{\mathrm{d}t}=\frac{k_2K_1K_2K_4[\mathrm{DPC}][\mathrm{OMH}][\mathrm{OH^-}][\mathrm{Ru(III)}]}{[\mathrm{H_3IO_6}^{2-}]+K_1[\mathrm{OH^-}][\mathrm{H_3IO_6}^{2-}]+K_1K_2[\mathrm{OH^-}]+K_1K_2K_4[\mathrm{OH^-}][\mathrm{OMH}]} \tag{12}$$

$$\frac{\mathrm{Rate}}{[\mathrm{DPC}]}=k_C=k_T-k_U=\frac{k_2K_1K_2K_4[\mathrm{OMH}][\mathrm{OH^-}][\mathrm{Ru(III)}]}{[\mathrm{H_3IO_6}^{2-}]+K_1[\mathrm{OH^-}][\mathrm{H_3IO_6}^{2-}]+K_1K_2[\mathrm{OH^-}]+K_1K_2K_4[\mathrm{OH^-}][\mathrm{OMH}]} \tag{13}$$

The rate law (13) can be rearranged into the following form which is suitable for verification:

$$\frac{[\mathrm{Ru(III)}]}{k_C} = \frac{[\mathrm{H_3IO_6}^{2-}]}{k_2K_1K_2K_4[\mathrm{OH}^-][\mathrm{OMH}]} + \frac{[\mathrm{H_3IO_6}^{2-}]}{k_2K_2K_4[\mathrm{OMH}]} + \frac{1}{k_2K_4[\mathrm{OMH}]} + \frac{1}{k_2} \qquad (14)$$

According to Eq. (14), other conditions being constant, plots of $[\mathrm{Ru(III)}]/k_C$ *vs.* $1/[\mathrm{OMH}]$, $1/[\mathrm{OH}^-]$ and $[\mathrm{H_3IO_6}^{2-}]$ should be linear and are found to be so (Fig. 8). The slopes and intercepts of such plots lead to the values of K_1, K_2, K_4 and k_2 (Table 4). The value of K_1 and K_2 are in good agreement with the literature [36]. Using these constants, the rate constants were calculated and compared with the experimental k_C values. There was a reasonable agreement with each other (Table 2), which fortifies the proposed mechanism (Scheme 2).

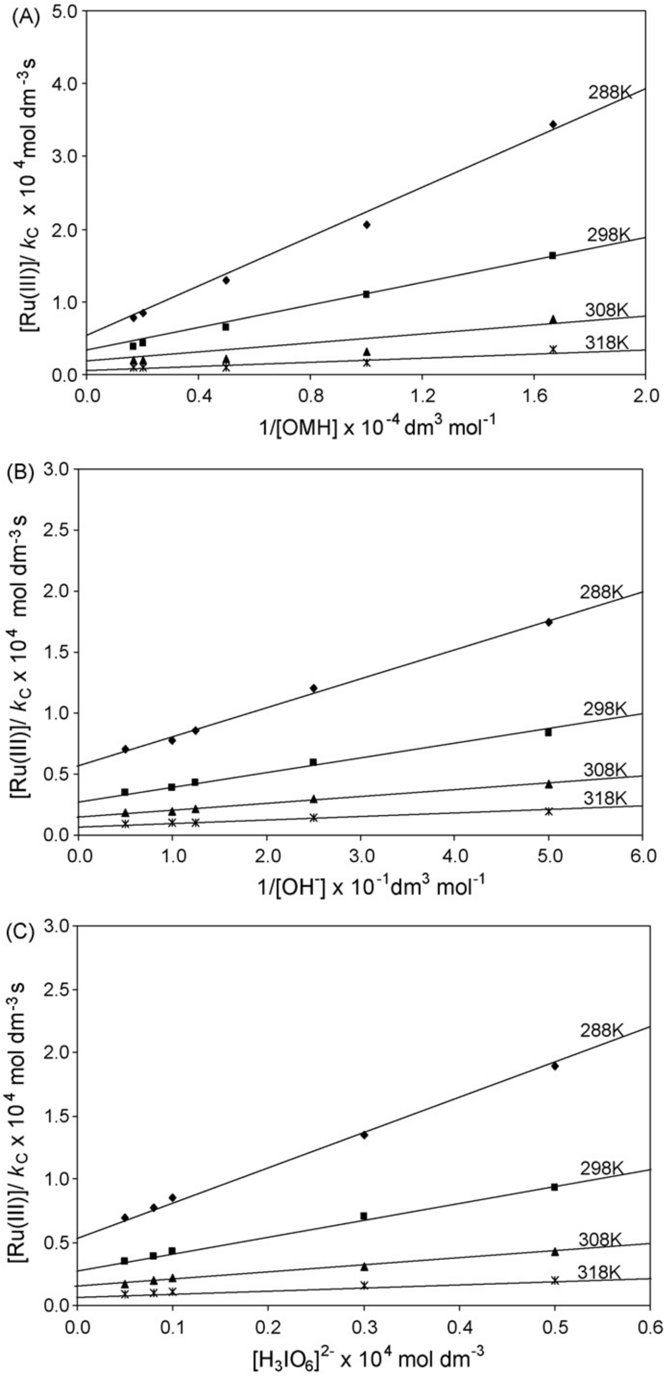


Fig. 8. Verification of rate law (13) for the Ru(III) catalyzed oxidation of DL-ornithine by diperiodatocuprate(III). Plots of (A) $[\mathrm{Ru(III)}]/k_C$ *vs.* $1/[\mathrm{OMH}]$, (B) $[\mathrm{Ru(III)}]/k_C$ *vs.* $1/[\mathrm{OH}^-]$ and (C) $[\mathrm{Ru(III)}]/k_C$ *vs.* $[\mathrm{H_3IO_6}]^{2-}$ at four different temperatures (conditions as in Table 2).

The negligible effect of ionic strength and dielectric constant of medium on the rate explains qualitatively the reaction between neutral and positively charged ions, as seen in Scheme 2. The thermodynamic quantities for the different equilibrium steps, in Scheme 2 can be evaluated as follows. The [OMH], $[\mathrm{OH}^-]$ and $[\mathrm{H_3IO_6}^{2-}]$ (Table 2) were varied at four different temperatures. The plots of $[\mathrm{Ru(III)}]/k_C$ *vs.* $1/[\mathrm{OMH}]$, $[\mathrm{Ru(III)}]/k_C$ *vs.* $1/[\mathrm{OH}^-]$ and $[\mathrm{Ru(III)}]/k_C$ *vs.* $[\mathrm{H_3IO_6}^{2-}]$ should be linear and are found to be so. From the slopes and intercepts, the values of K_1, K_2 and K_4 were calculated at four different temperatures. A vant Hoff's plot was made for the variation of K_1, K_2 and K_4 with temperature ($\log K_1$ *vs.* $1/T$, $\log K_2$ *vs.* $1/T$ and $\log K_4$ *vs.* $1/T$). The values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG were calculated for the first, second and third equilibrium steps. These values are given in Table 4. The negative value of $\Delta S^{\#}$ ($-11.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$) suggests that intermediate complex is more ordered than the reactants [39]. The observed modest enthalpy of activation and higher rate constant for the slow step indicate that the oxidation presumably occurs *via* an inner-sphere mechanism. This conclusion is supported by earlier observation [45,46]. The activation parameters evaluated for the catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction. The catalyst Ru(III) forms the complex (C_2) with substrate, which enhances the reducing property of substrate than that without catalyst. Further, the catalyst Ru(III) modifies the reaction path by lowering the energy of activation.

It is also interesting to note that the transient species involved in both the uncatalyzed and Ru(III) catalyzed reactions is different but leads to the formation of same products. The uncatalyzed reaction in alkaline medium has been shown to proceed via a MPC–OMH complex which decomposes slowly in a rate determining step to give the products via free radical in the further fast steps, where as, in the catalyzed reaction, it has been shown to proceed *via* Ru(III)–OMH complex which further reacts with one mole of MPC in the rate determining step to give the products via free radical in the further fast steps. Since in both the cases MPC and OMH were involved, the products obtained were same.

5. Conclusion

A comparative study of uncatalyzed and Ru(III) catalyzed oxidation of DL-ornithine by diperiodatocuprate(III) was studied. Among the various species of copper(III) in alkaline medium, $[\mathrm{Cu(H_2IO_6)(H_2O)_2}]$ is considered to be the active species for the title reaction. The active species of Ru(III) is found to be $[\mathrm{Ru(H_2O)_5OH}]^{2+}$. The reaction rates revealed that Ru(III) catalyzed reaction is about eight-fold faster than the uncatalyzed reaction. It becomes apparent that, in carrying out this reaction, the role of reaction medium is crucial. Activation parameters were evaluated for both catalyzed and uncatalyzed reactions. Catalytic constants and the activation parameters with reference to catalyst were also computed. The overall sequence described here is consistent with all the experimental evidences including the product, spectral, mechanistic and kinetic studies.

Appendix A.

Derivation of rate law for uncatalyzed reaction

According to Scheme 1:

$$\mathrm{Rate} = -\frac{d[\mathrm{DPC}]}{dt} = k_1[\mathrm{C_1}] = \frac{k_1K_1K_2K_3[\mathrm{DPC}][\mathrm{OMH}][\mathrm{OH}^-]}{[\mathrm{H_3IO_6}]^{2-}} \qquad (\mathrm{A.1})$$

The total concentration of $[\mathrm{DPC}]_T$ is given by,

$$\begin{aligned}[\mathrm{DPC}]_T &= [\mathrm{DPC}]_f + [\mathrm{Cu(H_2IO_6)(H_3IO_6)}]^{2-} \\ &\quad + [\mathrm{Cu(H_2IO_6)H_2O)_2}] + [\mathrm{C_1}]\end{aligned}$$

where *T* and *f* refer to total and free concentrations

$$[\mathrm{DPC}]_f = \frac{[\mathrm{DPC}]_T[\mathrm{H_3IO_6}]^{2-}}{[\mathrm{H_3IO_6}]^{2-} + K_1[\mathrm{H_3IO_6}]^{2-}[\mathrm{OH^-}] + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3[\mathrm{OH^-}][\mathrm{OMH}]} \qquad (\mathrm{A.2})$$

Similarly,

$$\begin{aligned}[\mathrm{OMH}]_T &= [\mathrm{OMH}]_f + \mathrm{C_1} \\ &= [\mathrm{OMH}]_f + \frac{K_1K_2K_3[\mathrm{DPC}]_f[\mathrm{OMH}]_f[\mathrm{OH^-}]_f}{[\mathrm{H_3IO_6}]^{2-}} \\ &= [\mathrm{OMH}]_f\left[1 + \frac{K_1K_2K_3[\mathrm{DPC}]_f[\mathrm{OH^-}]_f}{[\mathrm{H_3IO_6}]^{2-}}\right]\end{aligned}$$

In view of low concentration of [DPC] and $[\mathrm{H_3IO_6}]^{2-}$ second term can be neglected

$$[\mathrm{OMH}]_T = [\mathrm{OMH}]_f \qquad (\mathrm{A.3})$$

Similarly,

$$\begin{aligned}[\mathrm{OH^-}]_T &= [\mathrm{OH^-}]_f + [\mathrm{Cu(H_2IO_6)(H_3IO_6)}]^{2-} + [\mathrm{Cu(H_2IO_6)(H_2O)_2}] \\ &= [\mathrm{OH^-}]_f + K_1[\mathrm{OH^-}][\mathrm{DPC}] + \frac{K_1K_2[\mathrm{DPC}][\mathrm{OH^-}]}{[\mathrm{H_3IO_6}]^{2-}}\end{aligned}$$

In view of low concentration of [DPC] and $[\mathrm{H_3IO_6}]^{2-}$ used,

$$[\mathrm{OH^-}]_T = [\mathrm{OH^-}]_f \qquad (\mathrm{A.4})$$

Substituting the values of $[\mathrm{DPC}]_f$, $[\mathrm{OMH}]_f$ and $[\mathrm{OH^-}]_f$ in Eq. (A.1) and omitting subscripts, we have,

$$k_{\mathrm{U}} = \frac{\mathrm{Rate}}{[\mathrm{DPC}]} = \frac{k_1K_1K_2K_3[\mathrm{OMH}][\mathrm{OH^-}]}{[\mathrm{H_3IO_6}^{2-}] + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6}^{2-}] + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3[\mathrm{OH^-}][\mathrm{OMH}]}$$

The rate law for the ruthenium(III) catalyzed reaction was derived similarly.

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