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Impact of CPC micellar medium on Ru(III) promoted oxidation of L-Valine by diperiodatocuprate(III)

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The objective of the proposed investigation is to examine the influence of cationic surfactant on the Ru(III) facilitated L-Valine oxidation using diperiodatocuprate(III) (DPC) in an alkaline medium. The oxidation rate was ascertained by measuring the decrease in absorbance at a wavelength of 415 nm, an indicator of the Cu(III) concentration. The reaction's advancement was assessed employing the pseudo-first-order condition as a gauge for [OH^-], [DPC], ionic strength, [L-Valine], [Ru(III)], [IO_4^-], [Surfactant], and temperature. L-Valine and DPC interact stoichiometrically in a ratio of 1:4. Across the spectrum of concentrations examined, the reported reaction reflects less than unit order kinematics in relation to both [L-Valine], and [OH^-], first-order reliance on the [DPC] and [Ru(III)], and negative fractional-order for [IO_4^-]. A zero salt effect is suggested by the observed constancy in oxidation rate with the inclusion of electrolytes. The oxidation rate is significantly enhanced by Ru(III) solution (as a catalyst) at ppm concentration. Cetylpyridinium chloride (CPC) micellar media facilitates an additional enhancement in the rate of the desired reaction. CPC thus exhibits an excellent compatibility with Ru(III) for the L-Valine oxidation using (DPC).

Keywords: Surfactant, Micellar medium, Oxidation, Diperiodatocuprate(III), Ru(III) catalyzed, L-Valine

The oxidation process plays a significant role in the synthesis of organic compounds by creating new functional moieties or modifying existing functional groups in molecules. Organic chemistry offers a captivating exploration into the world of amino acids. Nucleotides, proteins, and polypeptides are involved in various metabolic processes, showcasing their vital importance[1-5]. To gain a deeper understanding of enzyme kinetics, it might be essential to extensively study the mechanisms of nonenzymatic chemical processes involved in amino acid oxidation[6-10]. Through different experimental settings, amino acids have undergone oxidation by a variety of reagents, often resulting in decarboxylation and deamination[11]. Nevertheless, the various reaction systems may advance through unique mechanisms. The oxidation of amino acids is particularly exciting due to the varied oxidation products that result from different oxidants.

The utilization of certain metal ions with higher valence states, such as Fe(III), Ce(IV), V(V), Cr(VI), Mn(VII), and Co(III), as prevalent oxidizing agents, has been firmly established for a considerable period of time[12-14]. However, the oxidative conversions employing such metal oxidants need to be carried out under some extreme conditions (elevated concentration of base or acid and higher temperatures)[14, 15]. It is noteworthy to highlight that among the metal oxidants used in various redox processes is Cu(III), the periodate complex of Cu(III) is frequently used as an oxidant[16-19]. The Diperiodatocuprate(III) complex, commonly referred to as DPC, is currently extensively utilized for redox transformations in environmentally friendly solvents. This oxidant possesses a distinctive characteristic as a one-electron oxidant, exhibiting a redox potential of approximately 1.20 V in a basic medium[20]. The utilization of DPC as an oxidizing agent in an alkaline solution is constrained to a handful of instances because of its inadequate stability and solubility in aquatic environments[21]. Copper complexes play a significant role in oxidation chemistry owing to their prevalence and importance in biological processes[22]. Because of the complex equilibrium involving distinct Cu(III) species, it is quite fascinating to identify the specific species responsible for the oxidation process[16-19]. DPC efficiently facilitated the oxidation of various organic compounds, including amines, amino acids, antibiotics, ketones, and alcohols, in an alkaline milieu[16-19, 23, 24]. However, the redox action of DPC in the micellar milieu has not received much attention in the literature up to this point[25-27].

Transition metals have been recognized for their ability to catalyze a wide range of redox processes due to their different states of oxidation. Transition metal ions, including iridium, chromium, palladium, osmium, copper, iron, and ruthenium, have gained significant attention as catalysts in different redox reactions, either individually or in binary combinations[28-30]. As a catalyst, Ru(III) is able to facilitate the oxidation of various inorganic and organic moieties. The mechanism of catalysis is contingent upon the experimental conditions, oxidant, and the characteristics of the substrate[31]. It has been demonstrated that metal ions can function as catalysts *via* multiple mechanisms, including the complex creation with the substrate, oxidizing the reactant directly, or generating free radicals. The involvement of Ru(III) catalysis in redox processes exhibits varying levels of intricacy, primarily through the creation of diverse intermediary complexes and the presence of ruthenium's varying oxidation states[11].

Surfactants have become quite popular in various industries because of their remarkable ability to self-assemble in solutions along with at interfaces[32]. Surfactants, with their amphiphilic structure consisting of a polar head group and a nonpolar chain, possess cooperative and associative behaviors that make them intriguing to researchers across various disciplines[33]. The surfactant's aquatic solution demonstrates electrolytic characteristics when present in low concentrations. Micellization takes place in an aqueous milieu due to the presence of a substrate containing hydrophobic as well as hydrophilic components. The concentration at which surfactants spontaneously generate micelles is designated as the critical micelle concentration (CMC)[34]. A number of variables influence the micellization process, including but not limited to additives, type of surfactant and its hydrophobic tail length, solvent type, pH, and temperature[35]. Ionic surfactant micellization typically involves two different kinds of interactions: hydrophobic interaction involving nonpolar tails and electrostatic repulsion involving polar head groups[34]. Micelles are typically uncomplicated spherical supramolecular structures that are created by amphiphiles in an aquatic environment. The micellar system typically appears visually uniform at a large scale because of the presence of colloidal-sized aggregates. However, in actuality, they are microscopically heterogeneous systems and serve as nanoreactors for various organic processes[36]. Micelles have the ability to either speed up or slow down a chemical reaction compared to a similar reaction carried out in an aquatic medium. Currently, aqueous micellar technology is effectively utilized for conducting numerous organic reactions in an aqueous micellar medium. Working with organic conversions in the aquatic micellar milieu offers a more environmentally friendly approach to chemical processes that could otherwise generate harmful byproducts[37]. The introduction of "green chemistry" has prompted numerous scientists to utilize water as the universal solvent due to the estimation that 80% of the waste from chemical manufacturing consists of organic solvents[38]. Another approach in green chemistry involves utilizing amphiphilic compounds that can form micelles which provide favorable conditions for the dissolution of insoluble organic substrates[39]. Because of the potentially highly efficient concentration of the reacting species within the micelle, the tested reaction rates may be faster compared to those typically seen in organic media. Micellar catalysis is the term for this concept, and numerous investigations in this area have been conducted[40]. Due to these benefits and aligning with the principles of nature's organic synthesis, physical chemists have chosen aqueous surfactant solutions as a more environmentally friendly reaction medium.

An analysis of existing literature indicates that there has been limited focus on the oxidation of organic compounds by DPC in a micellar environment[25-27]. Furthermore, there has been no investigation into the impact of metal catalysts on the oxidation of amino acids by DPC in a micellar environment. Research has shown that Ru(III) acts as a catalyst for the oxidation of amino acids by DPC in an alkaline environment[30, 31]. These studies are highly important for comprehending the mechanistic aspects of amino acids in redox reactions and determining the active species of Ru(III) catalyst and Cu(III). Additionally, understanding the impact of surfactants on reaction rates adds further significance to a comprehensive investigation of the title reaction. Therefore, the present study aims to explore the influence of cationic micellar environments on the catalytic oxidation of L-Valine by DPC using Ru(III) as the catalyst.

Experimental Section

Reagents and Chemicals

The kinetic experiment was conducted using analytical-grade reagents and double-deionized water over the entire study. Surfactant utilized, cetylpyridinium chloride (CPC) (Fisher Scientific, India), was of utmost purity. L-Valine (99%) was provided by Loba India, which was utilized without any further processing. $RuCl_3$ (Fisher Scientific, India) was dissolved in HCl to make a standard stock solution of Ru(III). EDTA titration was used to determine its concentration[41]. A standard protocol was followed in the preparation and standardization of the copper(III) periodate complex[42, 43]. The presence of the copper(III) complex was confirmed by the UV–Vis spectrum, demonstrating a maximum absorbance at 415 nm. Preparing a stock solution of periodate involved dissolving a measured amount of KIO_4 (HiMedia India) in hot water. The solution was then left to reach equilibrium for 24 hours before use. Its concentration was determined using iodometric analysis[44], while maintaining a neutral *p*H with the help of a phosphate buffer. The ionic strength of the reacting medium was maintained by employing KNO_3 (HiMedia India), while KOH (Merck, India) regulated the *p*H of the reacting solutions.

Apparatus

A Lab Junction *p*H Meter (model LJ-111) was employed to regulate the *p*H of the resultant mixture. The device's accuracy was confirmed using a recommended buffer solution. A T65 UV-visible spectrophotometer (double-beam) made by PG Instruments Limited was deployed for the acquisition of absorbance at a specified wavelength. An independently developed system of circulating water was responsible for maintaining a constant temperature inside the cell compartment. For the analysis of the ultimate oxidation product, the IR Tracer-100 FTIR spectrometer (Shimadzu, Japan) was utilized.

Kinetic Measurements

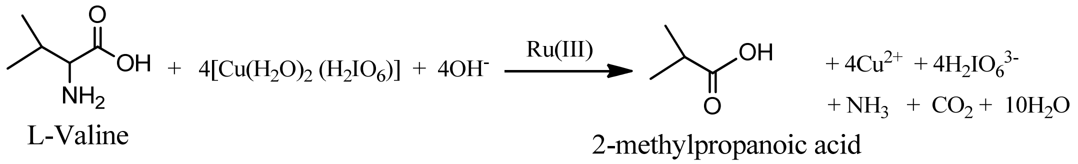
The reaction was thoroughly studied kinetically before the experimental conditions were set. No modifications were implemented to the absorption measurements as, when the DPC was excluded, no other intervening solutions demonstrated noticeable absorption at 415 nm wavelength. The oxidation of L-Valine by DPC, promoted by Ru(III), was observed under pseudo-first-order conditions ([L-Valine] > [DPC]) in both aqueous and micellar mediums at a temperature of 298 K. Thus, the reactants were pre-immersed in a thermostat for 30 minutes to maintain their temperature at 298 ± 0.1 K during each kinetic run. The oxidation reaction under investigation was conducted in an alkaline environment ($[OH^-] = 0.03$ M). The reactants with specified concentrations were scrupulously mixed in a precise sequence: L-Valine, KOH, KNO_3, Ru(III), and DPC to initiate the oxidation of L-Valine in both aqueous and surfactant medium. The monitoring of the reaction progress involved determining the decline in absorbance at 415 nm corresponding to DPC. Throughout the study, a consistent concentration of KIO_4 was employed during the kinetic runs. Testing was conducted to determine if the presence of excess periodate in DPC would cause oxidation of L-Valine. The results showed that there was not any substantial interference from KIO_4 under the conditions used in the experiment. The non-linear least squares fitting approach was utilized as a metric to compute the reaction's rate constant (k_{obs}).

Results

Stoichiometry and product analysis

Via monitoring the decline in absorption at 415 nm, the kinetic examination of Ru(III) promoted L-Valine oxidation by Cu(III) in a micellar environment was addressed. The Cu(III) reduction to Cu(II) is liable for the observed decrease in absorbance. Through careful observation, it was noted that the brown Cu(III) solution gradually transformed into a light blue hue. This change in color can be attributed to the development of Cu(II) species[19, 20], which further confirms the continuous advancement of the redox reaction. The aqueous and micellar medium were included in the kinetic study, which was carried out at 298 K under an alkaline condition utilizing 0.03 M KOH.

Pertaining to a specified quantity of Ru(III), KIO_4, and a 0.03 M KOH solution, the computed amount of DPC was allowed to react with an excess of L-Valine (tenfold) in a sealed vessel at 298 K. The reaction was allowed to conclude at that temperature. Unreacted DPC content was ascertained by means of spectrophotometric measurements performed at 415 nm. Based on the experimental outcomes, it can be observed that the chemical reaction between L-Valine and DPC proceeds in a 1:4 stoichiometric ratio, as demonstrated by equation 1.



(1)

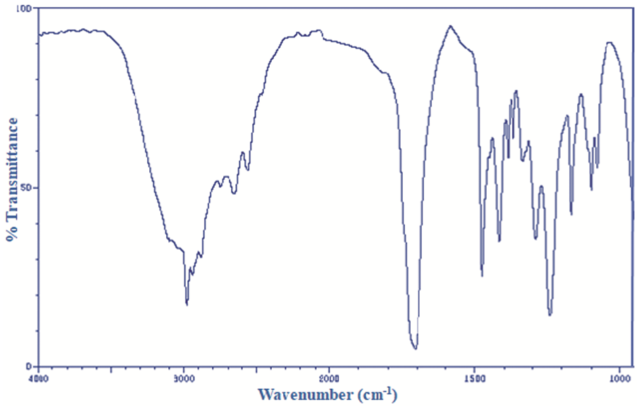


Fig. 1 — FTIR spectrum of the ultimate product (2-Methylpropanoic acid)

Once the reaction was finished, the mixture was transferred into a round bottle flask connected to a fractional distillation tube. The resulting distillation product was collected for subsequent analysis. The final product of the reaction was determined to be 2-methylpropanoic acid, and its identity was confirmed *via* FTIR spectral analysis.

T The FTIR spectra of the finished product (Fig. 1), 2-methylpropanoic acid, exhibit absorption peaks at 3300-2500 cm^{-1}, 2978, 2966, & 2878 cm^{-1}, and 1705 cm^{-1}. These spectral characteristics are associated with the stretching frequencies of the O-H bonds, C-H bonds, and the C=O bonds, respectively (Fig. 1). Moreover, the presence of a wide absorption band spanning from 2500 to 3300 cm^{-1} confirms the existence of the –COOH functional group.

An experiment was conducted to determine the presence of free radicals throughout the course of oxidation by means of a polymerization test. The reaction mixtures were kept in an inert environment for 6 hours with acrylonitrile scavenger of a specified quantity. The addition of methanol causes the formation of white solid particles, indicating the presence of free radicals in this reaction. The trials conducted without L-Valine under similar conditions were unsuccessful, suggesting that L-Valine is involved in the generation of free radicals.

Reaction Order

After mixing the reactants (L-Valine, KOH, KNO_3, Ru(III), IO_4^-, and DPC), the progress of L-Valine oxidation was monitored by computing the absorbance value at 415 nm. The observed rate constant (k_{obs}) was determined by plotting $\ln(A_\infty - A_t)$ against time. Where, A_t denotes absorbance at a specified time and A_∞represents absorbance after the completion of the reaction. The reaction orders were established by altering the concentrations of L-Valine, Ru(III), DPC, OH^-, and IO_4^- individually while maintaining the remaining components constant.

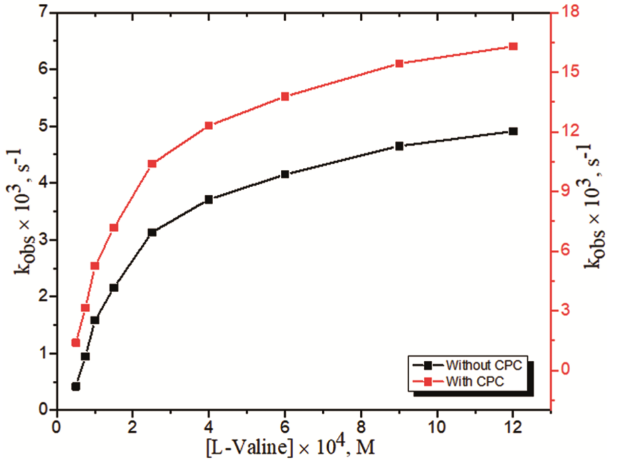


Fig. 2 — The correlation between [L-Valine] and k_{obs}at [DPC] = 1.5 × 10^{-5} M, $[OH^-]$ = 0.03 M, $[Ru^{3+}]$ = 1.5 × 10^{-6} M, I = 0.1 M (KNO_3), Temp = 298 K, $[IO_4^-]$ = 6.5 × 10^{-4} M, [CPC] = 6.5 × 10^{-4} M

Influence of varying [L-Valine] on oxidation rate

The impact of variable [L-Valine] upon the oxidation rate was investigated at a temperature of 298 K within the spectrum of 0.50 × 10^{-4} M to 12.0 × 10^{-4} M, at the specified OH^- concentration. The graph depicting the relationship between $k_{obs}$and [L-Valine] (Fig. 2) illustrates a rise in the reaction rate with [L-Valine]. The results of the investigation demonstrate that in both the aqueous and micellar environments, the L-Valine displays fractional-first-order kinetics. When compared to an aqueous medium, the micellar environment of CPC displays a higher rate of L-Valine oxidation by DPC catalyzed by Ru(III).

Influence of varying $[OH^-]$ on oxidation rate

Prior research on oxidizing the biological moieties employing DPC, whether catalyzed as well as unanalyzed, has established the crucial role of $[OH^-]$ in controlling the oxidation rate[16-20]. The study aimed to examine the reaction rate across a range of $[OH^-]$ from 0.01 M to 0.15 M *via* computing the rate constant at various $[OH^-]$ values. The reported reaction reflects fractional-first-order kinematics in relation to $[OH^-]$, as demonstrated by the relationship between $[OH^-]$ and k_{obs} in Fig. 3. At low levels of OH^-, the reaction rate is moderate, but then it gradually increases in a precise manner as the concentration of OH^- increases within the assessed range. Compared to an aqueous environment, the

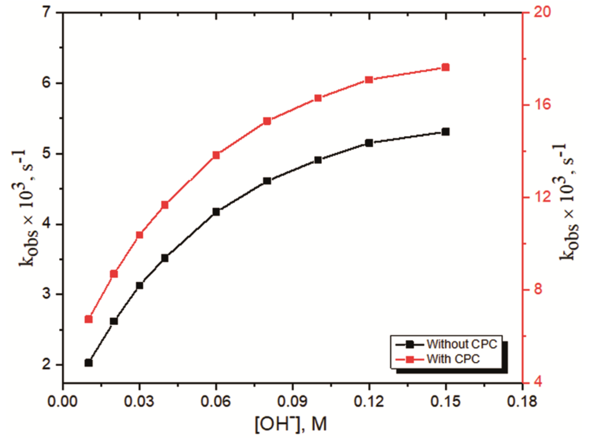


Fig. 3 — The correlation between $[OH^-]$ and k_{obs} at [DPC] = 1.5 × 10^{-5} M, [L-Valine] = 2.5 × 10^{-4} M, $[Ru^{3+}]$ = 1.5 × 10^{-6} M, I = 0.1 M (KNO_3), Temp = 298 K, $[IO_4^-]$ = 6.5 × 10^{-4} M, [CPC] = 6.5 × 10^{-4} M

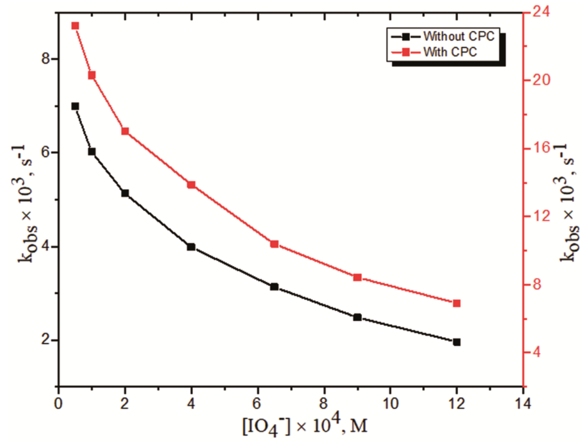


Fig. 4 — The correlation between $[IO_4^-]$ and k_{obs}at [DPC] = 1.5 × 10^{-5} M, [L-Valine] = 2.5 × 10^{-4} M, $[OH^-]$ = 0.03 M, $[Ru^{3+}]$ = 1.5 × 10^{-6} M, I = 0.1 M (KNO_3), Temp = 298 K, [CPC] = 6.5 × 10^{-4}

Table 1 — Effect of variation of [DPC] on rate constant (k_{obs}) at: [L-Valine] = 2.5 × 10^{-4} M, $[OH^-]$ = 0.03 M, $[Ru^{3+}]$ = 1.5 × 10^{-6}, I = 0.1 M (KNO_3), Temp = 298 K, $[IO_4^-]$ = 6.5 × 10^{-4} M, [CPC] = 6.5 × 10^{-4} M

[DPC] x 10^5M	k_{obs} x 10^3, s^{-1} (without CPC)	k_{obs} x 10^3, s^{-1} (with CPC)
1.5	3.13	10.39
3.0	3.18	10.49
6.0	3.09	10.45
9.0	3.16	10.33
12.0	3.10	10.37
15.0	3.07	10.41
20.0	3.15	10.35

oxidation rate in CPC micellar media was significantly higher, as depicted in Fig. 3. The observation is consistent with prior studies on the process of oxidizing organic compounds with the assistance of micellar catalysis[12-15].

Influence of varying [DPC] on oxidation rate

The oxidation rate was determined by utilizing the optimal conditions of [L-Valine] and OH^- while holding all other reaction parameters unchanged. The computation of the oxidation rate was performed with reference to [DPC] within the 1.5 × 10^{-5} M to 20.0 × 10^{-5} M concentration range. Referring to the calculated k_{obs} value for each [DPC], as shown in Table 1, it is apparent that the tested spectrum of [DPC] illustrates first-order kinetics in both aqueous and micellar milieu.

Influence of varying $[IO_4^-]$ on oxidation rate

To investigate the potential participation of IO_4^- in the oxidation process, the impact of incorporating IO_4^- into the reacting mixture was assessed while holding all other reaction parameters unchanged. It was observed that the reaction rate exhibited a decline as the concentration of IO_4^- increased (Fig. 4). In both aqueous and micellar medium, the order with respect to IO_4^- was found to be negative fractional. The micellar environment of CPC exhibits a higher rate of Ru(III)-catalyzed L-Valine oxidation by DPC than an aqueous medium does.

Influence of varying [Ru(III)] on oxidation rate

Considering the potential application of Ru^{3+}-catalyzed oxidation reactions for the detection of Ru(III) atthe micro level, it is crucial to examine the influence of $[Ru^{3+}]$ on the oxidation rate. The study focused on examining the oxidation rate within the range of 0.25 × 10^{-6} to 4.0 × 10^{-6} M [Ru(III)] under the most favorable reaction conditions. This was achieved by computing the rate constant (k_{obs}) at varying concentrations of Ru(III). Fig. 5 displays a linear trend between k_{obs} and [Ru(III)], which suggests first-order kinematics in reliance on [Ru(III)] across the concentration range under investigation.

Influence of varying [KNO_3] on oxidation rate

The influence of ionic strength, I, on the reaction rate was also investigated by controlling the reaction media's ionic strength between 0.05 - 0.50 M with potassium nitrate. The other reaction variables were remained constant at Temperature = 298 K, [L-Valine] = 2.5 × 10^{-4} M, $[OH^-]$ = 0.03 M, $[Ru^{3+}]$ = 1.5 × 10^{-6}, $[IO_4^-]$ = 6.5 × 10^{-4} M, [CPC] = 6.5 × 10^{-4} M, [DPC] = 1.5 × 10^{-5} M. A zero salt effect is suggested by the observed constancy in oxidation rate with increasing KNO_3 concentration, as displayed in Table 2. The constancy of the oxidation rate regardless of the ionic strength indicates the involvement of neutral species of Cu(III) in the rate-determining step.

Influence of varying temperature on oxidation rate

Temperature effects on oxidation rate were investigated within a 15-45°C range. Researchers neglected to investigate the reaction at higher temperatures because of concerns about the potential deterioration of the finished product and the extremely swift reaction rate. As anticipated, the reaction adhered to the Arrhenius equation, indicating that the reaction rate escalates as the temperature increases. At a temperature of 25°C, the reaction exhibits a fair rate of progression. Thus, it is suggested that a temperature of 298 K would be the optimal choice for conducting further research on the reaction system. The Arrhenius equation, by plotting $\ln k_{obs}$ against 1/T (Fig. 6), was employed for determining the energy of activation (E_a) and activation enthalpy ($\Delta H^{\#}$) values. They were discovered to be 38.86 ± 2.17 kJ $mole^{-1}$, 36.38 ± 1.99 kJ mole-1 in an aqueous environment, 33.65 ± 1.93 kJ $mole^{-1}$, and 31.17 ± 1.68 kJ $mole^{-1}$ in CPC micellar medium respectively.

Table 2 — Effect of variation of [Electrolyte] on rate constant (k_{obs}) at: [DPC] = 1.5×10^{-5} M, [L-Valine] = 2.5×10^{-4} M, $[OH^-]$ = 0.03 M, $[Ru^{3+}]$ = 1.5×10^{-6}, Temp = 298 K, $[IO_4^-]$ = 6.5×10^{-4} M, [CPC] = 6.5×10^{-4} M

I (KNO_3),M	k_{obs} x 10^3, s^{-1} (without CPC)	k_{obs} x 10^3, s^{-1} (with CPC)
0.05	3.16	10.42
0.10	3.13	10.39
0.20	3.10	10.45
0.30	3.08	10.48
0.40	3.06	10.35
0.50	3.15	10.37

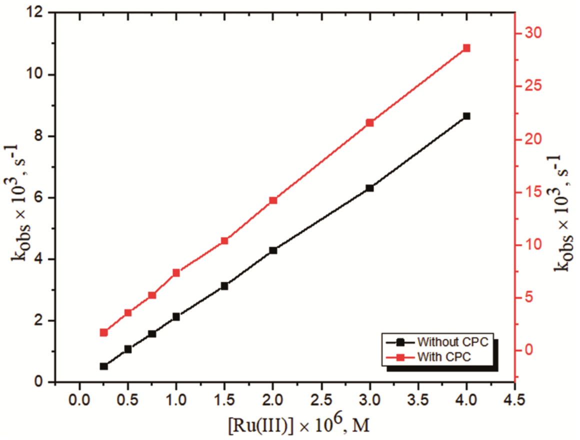


Fig. 5 — The correlation between [Ru(III)] and k_{obs}at [DPC] = 1.5×10^{-5} M, [L-Valine] = 2.5×10^{-4} M, $[OH^-]$= 0.03 M, I = 0.1 M (KNO_3), Temp = 298 K, $[IO_4^-]$ = 6.5×10^{-4} M, [CPC] = 6.5×10^{-4} M

Influence of varying [CPC] on oxidation rate

Surfactants possess the ability to induce rate enhancement in addition to homogenizing organic reactants in an aquatic medium, contingent on the charges they carry (neutral, cationic, and anionic)[12]. While keeping the other parameters constant, the concentration of CPC was varied from 0.25×10^{-4} M to 10.0×10^{-4} M to investigate its impact on the reaction rate. Based on the [CPC] against k_{obs} plot shown in Fig. 7, it is evident that the reaction rate experiences a rapid increase as the [CPC] increases up

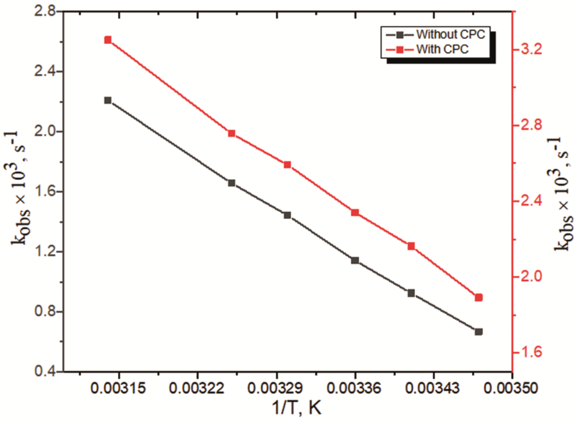


Fig. 6 — The correlation between Temperature and k_{obs}at [DPC] = 1.5×10^{-5} M, [L-Valine] = 2.5×10^{-4} M, $[OH^-]$ = 0.03 M, $[Ru^{3+}]$ = 1.5×10^{-6} M, I = 0.1 M (KNO_3), $[IO_4^-]$ = 6.5×10^{-4} M, [CPC] = 6.5×10^{-4} M

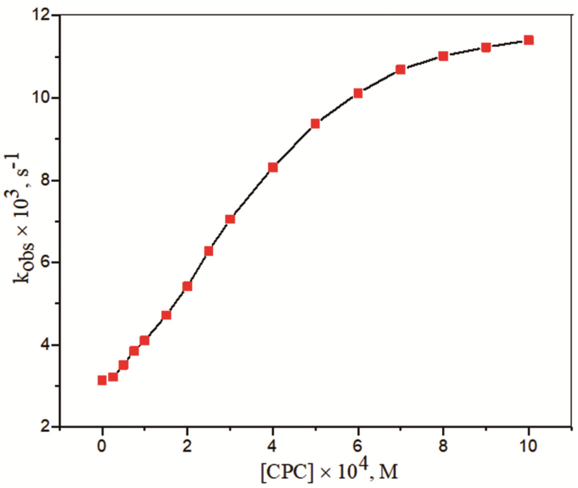


Fig. 7 — The correlation between [CPC] and k_{obs}at [DPC] = 1.5×10^{-5} M, [L-Valine] = 2.5×10^{-4} M, $[OH^-]$ = 0.03 M, $[Ru^{3+}]$ = 1.5×10^{-6} M, I = 0.1 M (KNO_3), Temp = 298 K, $[IO_4^-]$ = 6.5×10^{-4} M

to 6.0 × 10^{-4} M, which is approximately the CMC of CPC. Beyond this point, the oxidation rate continues to increase, but at a slower pace within the range of examined [CPC]. The calculated CMC of CPC in the observed reaction condition is 6.21 × 10^{-4} M, slightly lower than the value reported in the aquatic milieu. The intersection of the two linear lines on the k_{obs} *versus* [CPC] graph determines this.

Discussion

Mechanism and rate law

It has been reported that the copper(III) periodate complex, which is soluble in water, has the formula $[Cu(HIO_6)_2(OH)_2]$[7-45]. Periodate undergoes multiple equilibrium stages, as indicated by Eq. 2-4, contingent upon the *p*H of the medium[46].

$$H_5IO_6 \rightleftharpoons H_4IO_6^{-} + H^{+} \quad (2)$$

$$H_4IO_6^{-} \rightleftharpoons H_3IO_6^{2-} + H^{+} \quad (3)$$

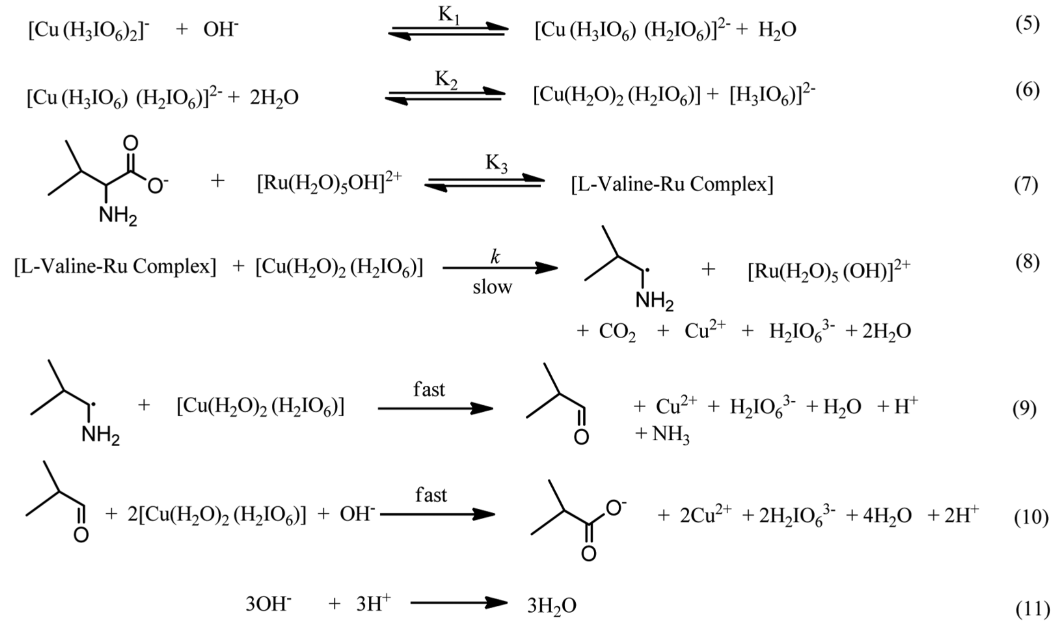
$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^{+} \quad (4)$$

Periodic acid is present as H_5IO_6 in an acidic environment and as $H_4IO_6^{-}$ at a *p*H of approximately 7. Therefore, in an alkaline environment, it is anticipated that the primary species will be $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$. Additionally, periodate is likely to dimerize at increased concentrations. However under the circumstances used for this kinetic investigation, the formation of such a species is negligible[18-20]. As a result, according to Eqs. 5 and 6, the soluble copper(III) periodate complex persists as either monoperiodatocuprate(III), $[Cu(H_2IO_6)(H_2O)_2]$, or diperiodatocuprate(III), $[Cu(H_2IO_6)(H_3IO_6)]^{2-}$, at the *p*H used in this investigation[47].

Ru(III) has demonstrated its efficacy as a catalyst in a wide range of redox reactions, whether in alkaline or acidic environments[9,12,19,20]. In an alkaline environment where $[OH^{-}] > [Ru(III)]$, Ru(III) primarily appears as its hydroxylated species ($[Ru(H_2O)_5OH]^{2+}$)[48]. Therefore, $[Ru(H_2O)_5OH]^{2+}$ is regarded as the reactive component of Ru(III) even under an alkaline CPC environment.

The results revealed that the addition of $[OH^{-}]$ increased the oxidation rate, while the introduction of periodate slowed it down. The [DPC] and the catalyst [Ru(III)] were found to have a direct impact (first-order) on the oxidation rate, while a more complex relationship (fractional order) was observed for [L-Valine] and $[OH^{-}]$. For the Ru(III) catalyzed oxidation of L-Valine in an alkaline environment, a recommended Scheme 1 has been put forward in order to clarify the witnessed orders. This scheme takes into account L-Valine as the anionic form of L-Valine.

Based on the observed impact of periodate on the oxidation rate. The species of interest of the copper(III) periodate complex is identified as mono-periodatocuprate(III) MPC. The findings indicate that the oxidation rate decreases with periodate concentration and increases with alkali concentration. This suggests



Scheme 1 — Mechanism of Ru(III) catalyzed oxidation of L-Valine by diperiodatocuprate(III) the existence of various copper(III) periodate complexes, as demonstrated in Eqs. (5) and (6). A zero salt effect, suggested by the observed constancy in oxidation rate with increasing KNO_3 concentration, provides a qualitative explanation for the reaction involving positively charged ions (L-Valine-Ru complex) and neutral species (MPC), as depicted in Scheme 1. This provides additional evidence supporting the presence of MPC as an active species of copper(III) periodate and the proposed mechanism.

The findings indicate that the oxidation of L-Valine by DPC in an alkaline milieu, catalyzed by Ru(III), occurs in a sequence of interconnected steps that culminate in the formation of a L-Valine-Ru intermediate complex (C_1), wherein L-Valine comes into contact with Ru(III) resulting in a complex (C_1) soluble in water. It is conceivable that the L-Valine-Ru complex will emerge during the equilibrium phase because the reaction rate displays a fractional-first-order correlation with [L-Valine]. The following step, which determines the rate, involves the reaction between the complex C_1 and MPC, resulting in the formation of free radical species of L-Valine. This reaction also results in the replenishment of the catalyst and the generation of Cu(II). The resulting free radical swiftly reacts with MPC, yielding the 2-methylpropanal. Furthermore, the 2-methylpropanal undergoes a reaction with two other molecules of MPC, resulting in the formation of 2-methylpropanoic acid as the final product.

The rate law for the proposed scheme can be determined as follows:

$$\text{Rate of Reaction} = -\frac{d\,[\mathrm{DPC}]}{dt} = k\,[\mathrm{Complex}][\mathrm{Cu(H_2O)_2\,(H_2IO_6)}] \quad ...(12)$$

Utilizing Equations 7, 8, and 9 we obtained,

$$\text{Rate of Reaction} = -\frac{d\,[\mathrm{DPC}]}{dt} = \frac{kK_1K_2K_3[\mathrm{L-Valine}]_F[\mathrm{Ru(III)}]_F[\mathrm{DPC}]_F[\mathrm{OH^-}]_F}{[\mathrm{H_3IO_6^{2-}}]} \quad ...(13)$$

The total [DPC] can be depicted as,

$$[\mathrm{DPC}]_T = [\mathrm{DPC}]_F + [\mathrm{Cu\,(H_2IO_6)(H_3IO_6)^{2-}}] + [\mathrm{Cu(H_2O)_2\,(H_2IO_6)}]$$

$$[\mathrm{DPC}]_T = [\mathrm{DPC}]_F + K_1[\mathrm{DPC}]_F[\mathrm{OH^-}] + \frac{K_1K_2[\mathrm{DPC}]_F[\mathrm{OH^-}]}{[\mathrm{H_3IO_6^{2-}}]}$$

$$[\mathrm{DPC}]_F = \frac{[\mathrm{DPC}]_T\,[\mathrm{H_3IO_6^{2-}}]}{[\mathrm{H_3IO_6^{2-}}] + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6^{2-}}] + K_1K_2[\mathrm{OH^-}]} \quad ...(14)$$

Similarly the total [Ru(III)] can be represented as,

$$[\mathrm{Ru(III)}]_T = [\mathrm{Ru(III)}]_F + [\mathrm{Ru(III)\ in\ Complex}]$$

$$[\mathrm{Ru(III)}]_T = [\mathrm{Ru(III)}]_F + K_3\,[\mathrm{L-Valine}]\,[\mathrm{Ru(III)}]_F$$

$$[\mathrm{Ru(III)}]_F = \frac{[\mathrm{Ru(III)}]_T}{1 + K_3[\mathrm{L-Valine}]} \quad ...(15)$$

Due to the low concentration of DPC and $H_3IO_6^{2-}$, we can consider,

$[\mathrm{L-Valine}]_T = [\mathrm{L-Valine}]_F$, and $[\mathrm{OH^-}]_T = [\mathrm{OH^-}]_F$

Considering the above condition and utilizing Equations 16, and 17, Equation 15 transforms to Equation 18,

$$\text{Rate} = \frac{kK_1K_2K_3\,[\mathrm{L-Valine}]\,[\mathrm{Ru(III)}]\,[\mathrm{DPC}]\,[\mathrm{OH^-}]}{\begin{array}{c}[\mathrm{H_3IO_6^{2-}}] + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6^{2-}}] \\ + K_1K_2[\mathrm{OH^-}] + K_3[\mathrm{L-Valine}][\mathrm{H_3IO_6^{2-}}] \\ + K_1K_3[\mathrm{L-Valine}][\mathrm{OH^-}][\mathrm{H_3IO_6^{2-}}] \\ + K_1K_2K_3[\mathrm{L-Valine}][\mathrm{OH^-}]\end{array}} \quad ...(16)$$

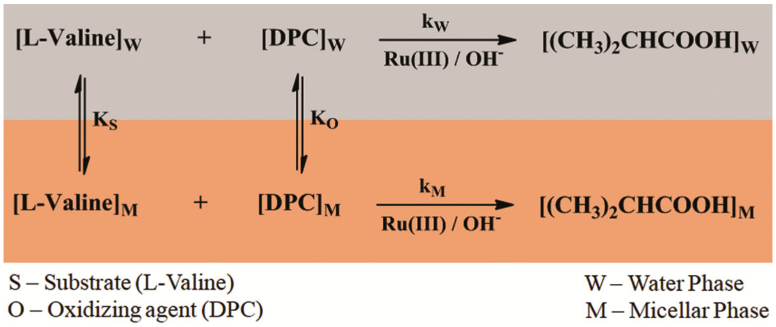
Due to the low concentration of periodate and L-Valine used in this study, we can neglect K_1K_3 [L-Valine][OH^-][$H_3IO_6^{2-}$], and K_3[L-Valine][$H_3IO_6^{2-}$], then the rate law will be,

$$\text{Rate} = \frac{kK_1K_2K_3\,[\mathrm{L-Valine}]\,[\mathrm{Ru(III)}]\,[\mathrm{DPC}]\,[\mathrm{OH^-}]}{\begin{array}{c}[\mathrm{H_3IO_6^{2-}}] + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6^{2-}}] \\ + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3[\mathrm{L-Valine}][\mathrm{OH^-}]\end{array}} \quad ...(17)$$

The above rate law describes all of the documented kinetic order with respect to distinct reaction parameters.

Role of surfactant (CPC) on oxidation rate

The dispersion of reactants in the micellar and aqueous pseudophases affects the progression of chemical reactions in a micellar media. Because of these intrinsic differences, these rates can be suppressed or accelerated[49-51]. Understanding the way, the different components interact with each other and how they affect the reaction rate is crucial. In this case, the electrostatic and hydrophobic interaction of the surfactant agglomerates with reactant molecules plays a significant role, as well as the changes they induce in the surrounding water molecules. At concentrations lower



Scheme 2 — Pseudophase model for the oxidation of L-Valine by DPC catalyzed in aqueous micellar medium

than the CMC, the monomeric surfactant displays catalytic characteristics. Catalytic micelles form through the aggregation of substrate and monomeric surfactant molecules, resulting in an acceleration of the reaction rate. The existence of premicellar states has a substantial impact on the rate of surfactant-facilitated processes[52, 53]. In contrast to micellar aggregates, the substrate in premicellar complexes is more reactive. After reaching the critical micelle concentration, the premicellar complexes disintegrate, resulting in the emergence of micelles[54]. This procedure efficiently maintains the rate of reaction.

The surfactant demonstrates an exceptional ability to form micelles at the nanoscale and facilitate the confluence of all involved constituents in the CPC micellar solution, thereby guaranteeing a smooth and enhanced reaction. Cetylpyridinium chloride (CPC), which is a cationic surfactant, forms micelles through a process called micellization. These micelles have a positively charged outer layer. Therefore, it should be forbidden for the cationic entities ($[Ru(H_2O)_5OH]^{2+}$) to have access to the substrate in the stern layer as well as the micellar interface[55]. Based on our understanding of chemistry, it is reasonable to assume that cationic entities will undergo hydroxylation in an alkaline environment and turn neutral. In the presence of OH^-, these neutral species are now capable of interacting with the surfactant *via* ion-dipole interactions and hydrogen bonding[9]. Within an alkaline CPC micellar environment, the micelles' highly positive-charged surface allows for the unhindered approach of the neutral MPC and Ru(III) as well as negatively charged OH^- ions towards the L-Valine molecule in the stern layer without encountering electrostatic repulsion. This leads to a spike in the effective collision frequency amongst the molecules involved in the reaction, resulting in an elevated reaction rate. CPC thus enhances and expedites the Ru(III) catalyzed oxidation of L-Valine by DPC in an alkaline environment.

The pseudophase model (Scheme 2) provides a suitable explanation for the oxidation reactions of L-Valine by DPC catalyzed by Ru(III) in aquatic micellar environments. Within this diagram, K_O and K_S represent the distribution coefficients of the DPC and L-Valine between the micellar and aqueous pseudophases. This model allows for the correlation of data to determine the oxidation rate constants and the relative abundance of reactants (DPC and L-Valine) within the pseudophases. The pseudophase model offers a comprehensive clarification of the total reaction rate, which is determined by the cumulative rates of each individual pseudophase. In this scenario, both L-Valine and DPC (oxidant) are distributed across both the micellar and aqueous phases. Due to the significantly higher rates observed in CPC micellar media ($k_M = 10.39 \times 10^{-3}\ s^{-1}$) compared to aqueous medium ($k_W = 3.13 \times 10^{-3}\ s^{-1}$), one can investigate and understand the mechanistic differences between the two. The disparity in the oxidation rate of L-Valine in micellar and aqueous phases provides evidence for the dispersion of reacting substances across two phases. Due to the more rapid increase in rate constant values in the micellar phase compared to the aqueous phase, it can be inferred that the micellar phase possesses a higher substrate concentration.

Conclusion

The present study contributes to our comprehension of the metal-promoted amino acid oxidation by DPC in a micellar environment. Across the spectrum of concentrations examined, the reported reaction reflects fractional-first-order kinematics with reliance on [L-Valine], and first-order reliance on the [DPC], and [Ru(III)]. The constant oxidation rate in the presence of electrolytes provides evidence in favor of a zero salt effect. OH^- plays a significant role in the reaction and adheres to the fractional-first-order kinematics. The observed decrease in reaction rate with [IO_4^-] injection, and zero salt effect strongly suggests the involvement of monoperiodatocuprate(III) as an oxidant. Surfactants, remarkable chemical entities, enhance the speed of various reactions. Metals, in conjunction with surfactants, have been utilized for decades to accelerate the rate of synthetic organic processes. In L-Valine oxidation by DPC in an alkaline environment, the inclusion of Ru(III) salt as a catalyst proves to be highly effective. The combination of CPC and Ru(III) further enhances the reaction rate, offering a greater catalytic effect than Ru(III) alone. Thus, when it comes to the L-Valine oxidation process using (DPC), CPC shows excellent compatibility with Ru(III).

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