Silver(I) and Copper(II) Catalysis for Oxidation of Histidine by Cerium(IV) in Acid Medium: A Comparative Kinetic Study

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ABSTRACT: The catalytic effect of silver(I) and copper(II) ions on the oxidation of histidine by cerium(IV) in aqueous sulfuric acid solutions was studied spectrophotometrically at a constant ionic strength of 3.0 mol dm^{-3} and at 25°C. In both uncatalyzed and metal ions-catalyzed paths, the reactions exhibited first-order kinetics with respect to [Ce(IV)] and [catalyst], and fractional first-order dependences with respect to [His] and [H^+]. The oxidation rates increased as the ionic strength and dielectric constant of the reactions media increased. The catalytic efficiency of Ag(I) was higher than that of Cu(II). Plausible mechanistic schemes for both uncatalyzed and catalyzed reactions were proposed, and the rate laws associated with the suggested mechanisms were derived. In both cases, the final oxidation products of histidine were identified as 2-imidazole acetaldehyde, ammonium ion, and carbon dioxide. The activation parameters associated with the second-order rate constants were evaluated. © 2017 Wiley Periodicals, Inc. Int J Chem Kinet 49: 143–156, 2017

INTRODUCTION

Ceric sulfate has been widely employed as an oxidant in the mechanistic studies in aqueous sulfuric acid medium [1–8] because of its stability and its availability. Cerium(IV) is less stable in aqueous nitric and perchloric acid solutions [9–12]. It was rarely used in perchloric acid medium due to the presence of dimers and polymers of it in such medium [11,12]. Identification of the kinetically active Ce(IV) species [2,3] is a problem during studies of the kinetics and mechanisms of cerium(IV) oxidation in aqueous sulfuric acid solutions using different types of organic and inorganic

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substrates. In aqueous sulfuric acid solutions, cerium(IV) can exist as a mixture of different types of sulfate species such as $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$, and $H_3Ce(SO_4)_4^-$ [1–5].

The amino acid histidine (His) was used to treat various diseases, and deficiency of it in hemoglobin can cause poor hearing. Histidine is very important because the body uses it to manufacture of histamine, which is responsible for a wide range of physiological processes. It provides metal-binding sites on many enzymes and is directly involved in catalysis. It also forms complexes with some transition metal ions in aqueous media [13,14]. The oxidation of histidine by different oxidants has been previously studied in different media [13–19], and in most cases the main oxidation product of histidine was 2-imidazole acetaldehyde.

A literature survey revealed no work has been done on the kinetics and mechanism of oxidation of histidine by cerium(IV) in the absence or presence of a catalyst. This leads us to investigate the kinetics and mechanistic aspects of the oxidation of this amino acid by cerium(IV) in aqueous sulfuric acid solutions in the absence and presence of two different metal ions catalysts, namely silver(I) and copper(II). We aim to investigate the selectivity of histidine toward cerium(IV) in sulfuric acid solutions, to understand the active species of the oxidant in this medium, to check the catalytic activity of Ag(I) and Cu(II) catalysts toward histidine oxidation, and to elucidate plausible reaction mechanisms.

EXPERIMENTAL

Materials and Methods

Materials. A stock solution of histidine was freshly prepared by dissolving the required amount of the sample (Merck, Germany; 99.3%) in double-distilled water. A solution of cerium(IV) was prepared by dissolving ceric ammonium sulfate (Sigma-Aldrich, Louis, USA; ≥99%) in a 1.0 mol dm^{-3} sulfuric acid solution (Merck), then diluting with double-distilled water. The concentration of cerium(IV) solution was determined by titrating it against ferrous ammonium sulfate solution. The solution of cerium(IV) was stored in the dark and was used after 24 h, since hydrolysis is negligible or ruled out after 12 h of preparation [20]. Cerium(III) solution was prepared by dissolving cerium(III) acetate (S.D. Fine Chem, Germany) in double-distilled water. Other chemicals and reagents such as sulfuric acid, sodium sulfate, hydrated copper sulfate, silver nitrate, acrylonitrile, and methanol used were of analytical grade with about 99.9% purity.

Kinetic Measurements. The rates of disappearance of cerium(IV) in aqueous sulfuric acid solution for uncatalyzed and catalyzed reactions were followed under conditions in which [His] ≫ [Ce(IV)]. The ionic strength was maintained constant (adjusted to 3.0 mol dm^{-3}) by the addition of sodium sulfate electrolyte. The oxidation reactions were carried out in a thermostated cell compartment at a fixed temperature (25°C), which was controlled to within ± 0.1°C. The reactions were initiated by mixing thermally preequilibrated solutions prepared under predetermined conditions. Ce(IV) solution was then added to the reaction vessel to initiate the oxidation process. The progress of the reactions was followed by monitoring the decay of cerium(IV) absorbance as a function of time at its absorption maximum, $\lambda = 316$ nm. The absorbance measurements were conducted on a temperature-controlled Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer (Japan). First-order plots of ln(absorbance) versus time were straight lines up to about 80% of the reaction completion. The pseudo–first-order rate constants (k_U and k_C) were determined as the slopes of these plots, and average values of at least two independent kinetic measurements were taken for calculation of the rate constants.

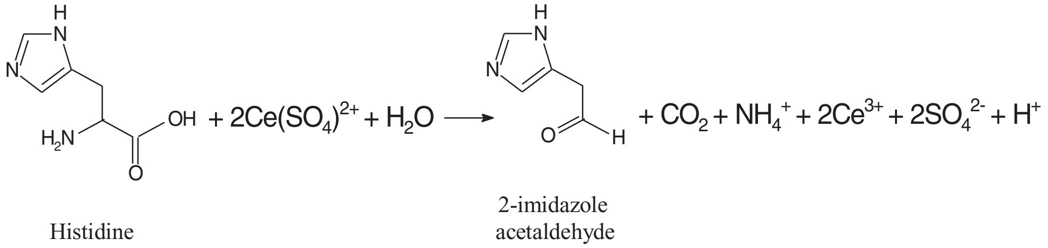
Whereas the reaction between cerium(IV) and histidine in sulfuric acid solution proceeded with a measurable rate in the absence of metal ions catalysts, the catalyzed reactions were thought to proceed in a parallel path, with contributions from both uncatalyzed and catalyzed oxidation reactions. Hence, the total rate constant (k_T) equals $k_U + k_C$.

A few kinetic runs were carried out after bubbling with purified nitrogen. The results of these runs were compared with those conducted under air. The results were the same, suggesting that the dissolved oxygen did not affect the rate constants.

RESULTS

Stoichiometry and Product Identification

The stoichiometry, determined spectrophotometrically and by titration, indicates the consumption of two Ce(IV) ions per one molecule of histidine yielding the final oxidation products as illustrated in the following equation:



(1)

Equation (1) is consistent with the results of product analysis. The product, 2-imidazole acetaldehyde, was estimated quantitatively by its 2,4-dinitrophenylhydrazine derivative [21]. Other products were identified as discussed earlier [22]. Similar oxidation products were obtained in the oxidation of histidine by other oxidants [13–15,17].

Spectral Changes

The spectral changes during the oxidation of His by cerium(IV) in sulfuric acid solutions in the presence of Ag(I) and Cu(II) catalysts are illustrated in Figs. 1a and 1b. In both cases, the spectra indicate gradual disappearance of the Ce(IV) band at its absorption maximum as a result of its reduction to Ce(III). It can be observed that the disappearance of Ce(IV) band in the presence of Ag(I) occurs faster than that in the presence of Cu(II).

Order of Reactions

The order of both uncatalyzed and catalyzed reactions with respect to the reactants was determined from the slopes of the plots of $\log k_U$ and $\log k_C$ versus log(concentration) by varying the concentrations of substrate, acid, and catalyst, in turn, while keeping all other conditions constant.

The concentration of the oxidant, cerium(IV), was varied in both reactions in the range of 0.5×10^{-4} to 5.0×10^{-4} mol dm^{-3}, keeping all other variables constant. The plots of ln(absorbance) versus time were found to be linear to almost 80% of the reactions completion. Furthermore, an increase in the initial oxidant concentration did not alter the oxidation rates of His (Table I). These results indicate that the order of reactions with respect to [Ce(IV)] is one.

The observed rate constants were determined at different initial concentrations of His, while other variables were kept constant. Increasing [His] increased the oxidation rates (Table I). Plots of the observed rate constants versus [His] were linear with positive intercepts as shown in Fig. 2, confirming fractional-first-order dependencies with respect to [His].

To study the effect of the hydrogen ion concentration on the oxidation rates, kinetic runs were carried out by varying the hydrogen ion concentration (0.5–3.0 mol dm^{-3}) using sulfuric acid and keeping other reactants concentrations constant. The rates of both uncatalyzed and catalyzed oxidation reactions were found to increase with increasing [H$^+$], as listed in Table I. Plots of k_U and k_C versus [H$^+$] were linear with positive

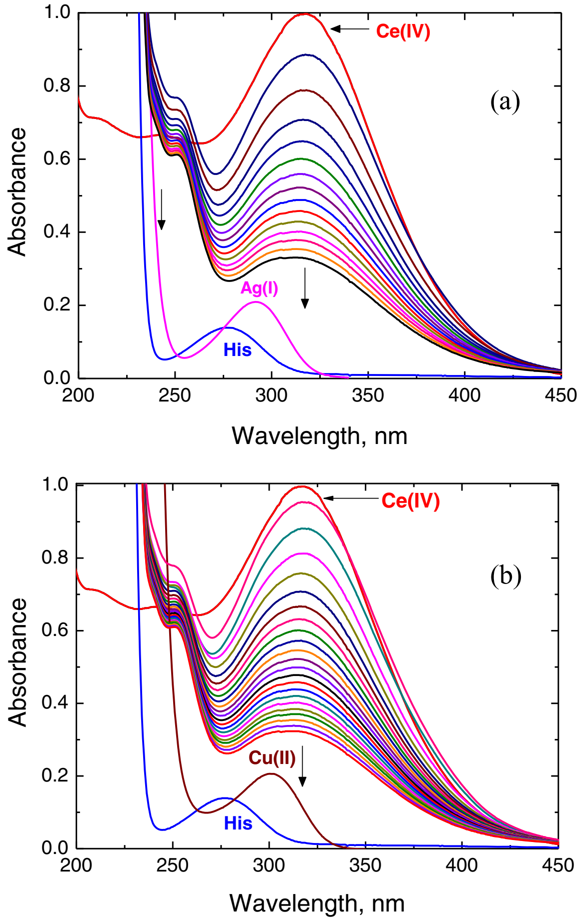


Figure 1 Spectral changes during silver(I)- and copper(II)-catalyzed oxidations of histidine (His) by cerium(IV) in sulfuric acid solutions. [His] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, [H$^+$] = 2.0, I = 3.0, [Ag(I)] = 8.0×10^{-6}, and [Cu(II)] = 8.0×10^{-4} mol dm^{-3} at 25°C. Scan time intervals = 1 min. [Color figure can be viewed at wileyonlinelibrary.com]

Table I Effect of Varying [Ce(IV)], [His], [H^+], [M(Y)], and Ionic Strength, I, on the First-Order Rate Constants in the Uncatalyzed and Silver(I)- and Copper(II)-catalyzed Oxidations of Histidine by Cerium(IV) in Sulfuric Acid Solutions at 25°C

					$10^5\ k$ (s^{-1})				
						Ag(I)		Cu(II)	
10^4 [Ce(IV] (mol dm^{-3})	10^3 [His] (mol dm^{-3})	[H^+] (mol dm^{-3})	*10^X[M(Y)] (mol dm^{-3})	I (mol dm^{-3})	k_U	k_T	k_C	k_T	k_C
0.5	6.0	2.0	8.0	3.0	62.3	279.9	217.6	182	119.7
1.0	6.0	2.0	8.0	3.0	64.4	288.9	224.5	188.4	124.0
2.0	6.0	2.0	8.0	3.0	64.0	290.3	226.3	186.4	122.4
3.0	6.0	2.0	8.0	3.0	65.7	293.8	228.1	190.9	125.2
4.0	6.0	2.0	8.0	3.0	63.9	294.3	230.4	185.5	121.6
5.0	6.0	2.0	8.0	3.0	63.4	294.0	230.6	183.7	120.3
2.0	2.0	2.0	8.0	3.0	33.8	165.1	131.3	105.0	71.2
2.0	4.0	2.0	8.0	3.0	49.7	235.2	185.5	149.1	99.4
2.0	6.0	2.0	8.0	3.0	64.0	290.3	226.3	186.4	122.4
2.0	8.0	2.0	8.0	3.0	76.1	339.7	263.6	220.4	144.3
2.0	10.0	2.0	8.0	3.0	85.0	410.3	325.3	255.3	170.3
2.0	12.0	2.0	8.0	3.0	94.9	449.8	354.9	301.1	206.2
2.0	6.0	0.5	8.0	3.0	23.0	119.3	96.3	73.2	50.2
2.0	6.0	1.0	8.0	3.0	37.4	173.8	136.4	112.3	74.9
2.0	6.0	1.5	8.0	3.0	51.1	233.0	181.9	139.4	88.3
2.0	6.0	2.0	8.0	3.0	64.0	290.3	226.3	186.4	122.4
2.0	6.0	2.5	8.0	3.0	81.0	352.2	271.2	222.2	141.2
2.0	6.0	3.0	8.0	3.0	90.9	414.9	324.0	264.2	173.3
2.0	6.0	2.0	2.0	3.0	64.0	118.3	54.3	96.3	32.3
2.0	6.0	2.0	4.0	3.0	64.0	175.0	111.0	122.1	58.1
2.0	6.0	2.0	6.0	3.0	64.0	244.9	180.9	154.5	90.5
2.0	6.0	2.0	8.0	3.0	64.0	290.2	226.2	186.4	122.4
2.0	6.0	2.0	10.0	3.0	64.0	345.6	281.6	220.2	156.2
2.0	6.0	2.0	12.0	3.0	64.0	428.1	364.1	242.7	178.7
2.0	6.0	2.0	8.0	3.0	64.0	290.2	226.2	186.4	122.4
2.0	6.0	2.0	8.0	3.3	67.2	301.9	234.7	194.3	127.1
2.0	6.0	2.0	8.0	3.6	70.8	316.9	246.1	202.1	131.3
2.0	6.0	2.0	8.0	3.9	74.7	328.9	254.2	211.1	136.2
2.0	6.0	2.0	8.0	4.2	78.3	340.3	262.3	217.7	139.4
2.0	6.0	2.0	8.0	4.5	81.4	352.7	271.3	225.4	144.0

Experimental error = ±4%.

*X = 6.0 for Ag(I) and X = 4.0 for Cu(II).

slopes (Fig. 3), suggesting that the orders with respect to [H^+] were less than unity.

To evaluate the reactions orders with respect to the concentrations of Ag(I) and Cu(II) catalysts, the oxidation rates were measured at various [M(Y)], (2.0–12.0) × 10^{-6} mol dm^{-3} for Ag(I) and (2.0–12.0) × 10^{-4} mol dm^{-3} for Cu(II), while other variables were kept constant. The reaction rate increased as [M(Y)] increased (Table I). The orders with respect to Ag(I) and Cu(II) were less than unity, as determined from the plots of log k_C versus log [M(Y)], as shown in Fig. 4.

Effect of Ionic Strength and Dielectric Constant

The effect of ionic strength on the rates of uncatalyzed and catalyzed reactions was studied by varying the ionic strength in the range of 3.0–4.5 mol dm^{-3} using sodium sulfate solution while maintaining the concentrations of all other reactants constant. Increasing ionic strength of the medium increased the oxidation rates of both reactions, and the Debye–Huckel plots were linear with positive slopes as illustrated in Fig. 5a.

To determine the effect of dielectric constant (D) of the medium on the oxidation rates, the reactions

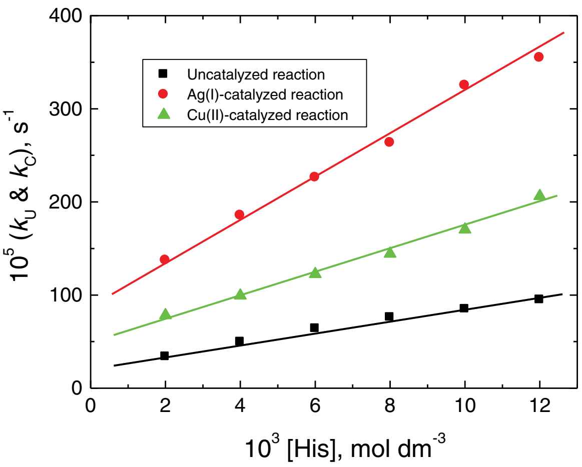


Figure 2 Effect of [His] on the rate constants in the uncatalyzed and metal ions–catalyzed oxidations of histidine by cerium(IV) in sulfuric acid solutions. [Ce(IV)] = 2.0×10^{-4}, [H^+] = 2.0, I = 3.0, [Ag(I)] = 8.0×10^{-6} and [Cu(II)] = 8.0×10^{-4} mol dm^{-3} at 25°C. [Color figure can be viewed at wileyonlinelibrary.com]

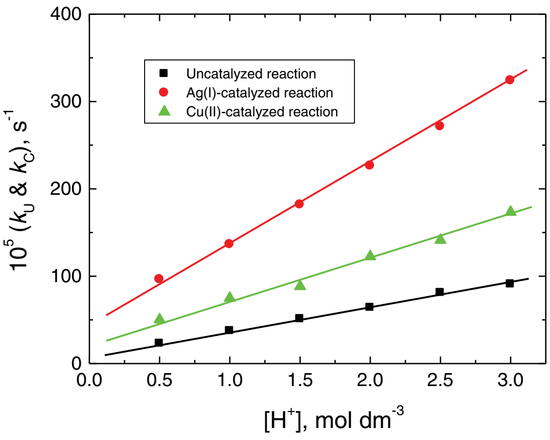


Figure 3 Effect of [H^+] on the rate constants in the uncatalyzed and metal ions–catalyzed oxidations of histidine by cerium(IV) in sulfuric acid solutions. [His] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, I = 3.0, [Ag(I)] = 8.0×10^{-6}, and [Cu(II)] = 8.0×10^{-4} mol dm^{-3} at 25°C. [Color figure can be viewed at wileyonlinelibrary.com]

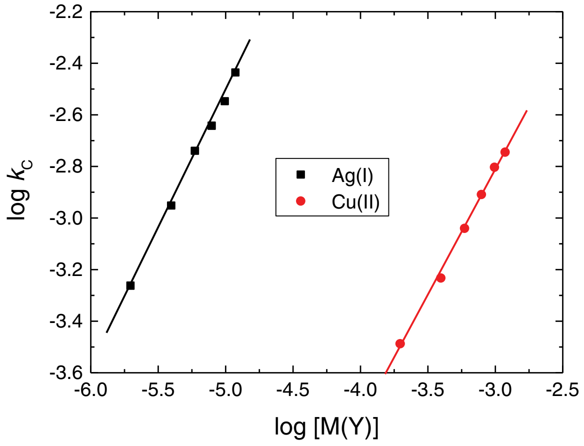


Figure 4 Plots of log k_C versus log M(Y) in the metal ions–catalyzed oxidations of histidine by cerium(IV) in sulfuric acid solutions. [His] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, [H^+] = 2.0, and I = 3.0 mol dm^{-3} at 25°C. [Color figure can be viewed at wileyonlinelibrary.com]

were studied at different solvent compositions (vol%) of acetic acid and water. At different compositions, the dielectric constant of the medium was calculated using the equation of Laidler and Eyring [23]: $D = D_1V_1 + D_2V_2$, where V_1 and V_2 are volume fractions, and D_1 and D_2 are dielectric constants of water and acetic acid as 78.5 and 6.15 at 25°C, respectively. The rate constants clearly decreased with decreasing dielectric constant of the solvent (i.e., increasing acetic acid content). Plots of log k_U and log k_C versus $1/D$ were linear with negative slopes (Fig. 5b).

Effect of [HSO_4^-]

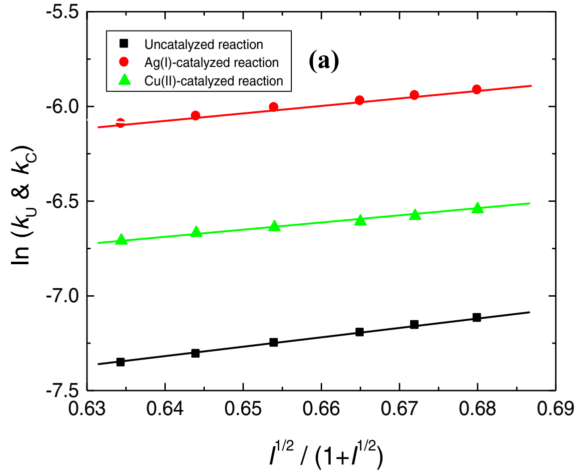
To study the effect of the bisulfate ion on the reaction rate, the oxidation reaction was carried out at concentrations of bisulfate in the range of 1.0–3.5 mol dm^{-3}, keeping the concentrations of all other reactants constant. It was observed that increasing the bisulfate concentration decreases the reaction rate, and the order with respect to [HSO_4^-] was negative. This is confirmed by the linear plot of $1/k_U$ versus [HSO_4^-] with a positive intercept, as shown in Fig. 6. Therefore, [HSO_4^-] shows a rate-retarding effect.

Effect of Initially Added Product

The effect of added cerium(III) was studied over the concentration range of 0.5×10^{-4} to 6.0×10^{-4} mol dm^{-3} at fixed concentrations of other reactants. Ce(III) did not have a significant effect on the oxidation rates of both uncatalysed and catalyzed reactions.

Effect of Temperature

The oxidation rates of both uncatalyzed and metal ions–catalyzed paths were measured at five different temperatures (288–308 K) at constant concentrations of the reactants. The results indicate that the rate constants increased with raising temperature. The activation parameters of the second-order rate constants, k'



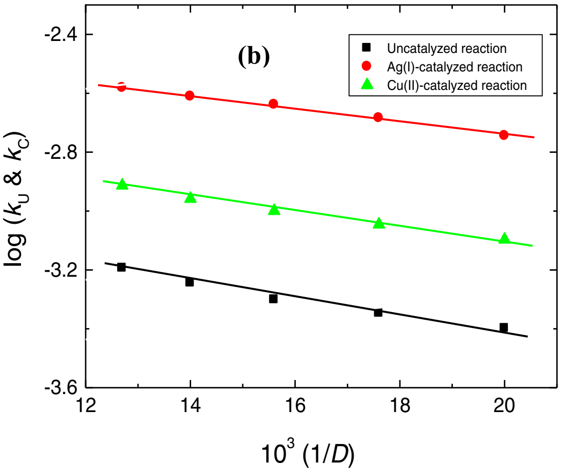


Figure 5 Effect of (a) ionic strength and (b) dielectric constant of the reaction medium on the rate constants in the uncatalyzed and metal ions–catalyzed oxidations of histidine by cerium(IV) in sulfuric acid solutions. [His] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, [H^+] = 2.0, [Ag(I)] = 8.0×10^{-6}, and [Cu(II)] = 8.0×10^{-4} mol dm^{-3} at 25°C. [Color figure can be viewed at wileyonlinelibrary.com]

($k' = k$/[His], where k is k_U or k_C) were calculated using Arrhenius (Fig. 7a) and Eyring (Fig. 7b) plots and are listed in Table II.

Test for Free Radical Intermediates

The generation of free radicals during a reaction was examined by a polymerization test. Known quantities of acrylonitrile scavenger were added to samples of the reaction mixtures that had been kept in inert atmosphere for 2 h. White precipitates (as a result of acrylonitrile polymerization) were formed upon diluting the reaction mixtures with methanol indicating free radicals intervention in the reactions. When the experiments were repeated in the absence of His under similar conditions, the tests were negative. These tests indicated that the reactions proceeded through free radical paths.

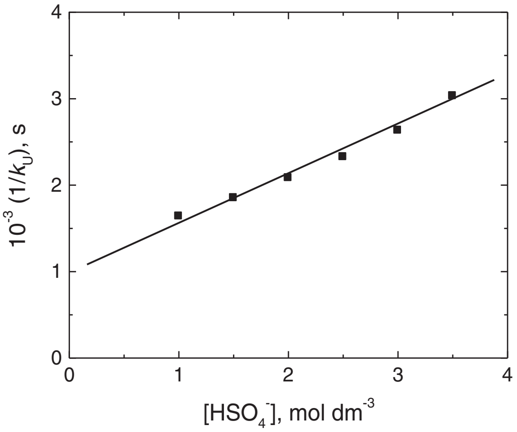


Figure 6 A plot of 1/k_U versus [HSO_4^-] in the uncatalyzed oxidation of histidine by cerium(IV) in sulfuric acid solution. [His] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, [H^+] = 2.0, and I = 3.0 mol dm^{-3} at 25°C.

DISCUSSION

It was reported [13,14,24] that amino acids tend to protonate at higher acid concentrations. In the present investigation, the high concentration of hydrogen ions used, as well as the significant increase in the oxidation rates upon increasing the acid concentration suggested protonation of histidine before its reaction with the oxidant, as represented by Eq. (3) in Scheme 1. Therefore, the protonated form of histidine (His^+) is suggested to be the kinetically reactive species in the rate-determining step.

On the other hand, in a sulfuric acid medium [3,4], cerium(IV) forms several sulfate complexes having an increasing number of coordinated sulfate ions according to the equilibria shown in Eqs. (A)–(C) [20,25],

$$Ce^{4+} + HSO_4^- \rightleftharpoons Ce\,(SO_4)^{2+} + H^+ \quad Q_1 = 3500 \tag{A}$$

$$CeSO_4^{2+} + HSO_4^- \rightleftharpoons Ce\,(SO_4)_2 + H^+ \quad Q_2 = 200 \tag{B}$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons Ce(SO_4)_3^{2-} + H^+ \quad Q_3 = 20 \tag{C}$$

The equilibrium constants, Q_1, Q_2, and Q_3, are given at an ionic strength of 2.0 mol dm^{-3} and 25°C.

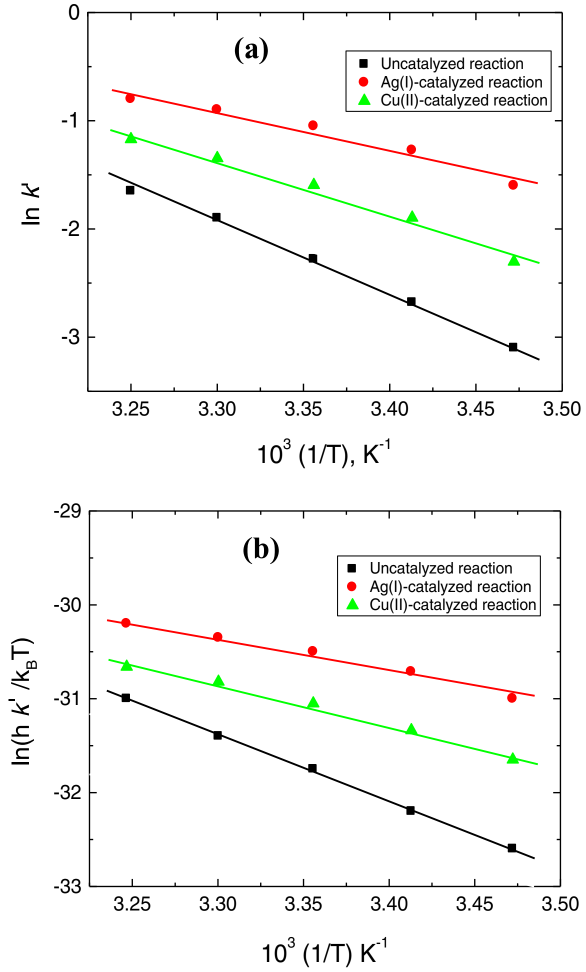


Figure 7 (a) Arrhenius and (b) Eyring plots in the uncatalyzed and metal ions–catalyzed oxidations of histidine by cerium(IV) in sulfuric acid solutions. [His] = 6.0 × 10^{-3}, [Ce(IV)] = 2.0 × 10^{-4}, [H^+] = 2.0, I = 3.0, [Ag(I)] = 8.0 × 10^{-6}, and [Cu(II)] = 8.0 × 10^{-4} mol dm^{-3}. [Color figure can be viewed at wileyonlinelibrary.com]

Based on the effect of [H^+] and [HSO_4^-] on the rate of the oxidation, one of these species was treated as the kinetically active species for cerium(IV). The observation in our work that HSO_4^- ions retard the rate of oxidation while increasing the rate as [H^+] increases, point to the fact that $Ce(SO_4)^{2+}$ may be the kinetically active species for cerium(IV) sulfate complexes. This case corresponds to Eq. (3) [20]. Also, because the rate constants increased upon increasing the ionic strength and dielectric constant of the reactions media, it is likely that $Ce(SO_4)^{2+}$ is one of the reactive species in these reactions, as reactions were suggested [26,27] to occur between two similarly charged species, that is, between His^+ and $Ce(SO_4)^{2+}$.

In earlier work [28], it was reported that a reaction rate that decreases as the concentration of HSO_4^- increases means that $Ce(SO_4)^{2+}$ and $Ce(SO_4)_2$ are kinetically active in the reaction, but the kinetic contribution of $Ce(SO_4)_2$ is negligibly small and the major active species is $Ce(SO_4)^{2+}$. Furthermore, electron flow toward the Ce(IV) center in $Ce(SO_4)^{2+}$ is favored over $Ce(SO_4)_2$ because the Ce(IV) centered in $Ce(SO_4)^{2+}$ bears a more positive charge. $Ce(SO_4)^{2+}$ species has also been suggested in earlier works [28–31].

Mechanism of Uncatalyzed Oxidation

The results of the kinetic study of the oxidation of His by cerium(IV) in sulfuric acid medium suggests formation of an intermediary complex between the protonated histidine, His^+, and the kinetically active species of Ce(IV), $Ce(SO_4)^{2+}$. Formation of an intermediary complex is supported by the less than unit order with respect to [His]. Complex formation was also proved kinetically by the nonzero intercept of the plot of $1/k_U$ versus 1/[His] (Fig. 8). This kinetic result favors the possible formation of an intermediary complex between the oxidant and substrate [32]. Furthermore, complex formation was supported by the obtained negative value of the entropy of activation, $\Delta S^{\#} = -94.04$ J K^{-1} mol^{-1}, which corresponds to the decrease in the degrees of freedom accompanying the transition from the initial state to the transition state [33,34]. The positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate endothermic formation of the intermediary complex and its nonspontaneity, respectively.

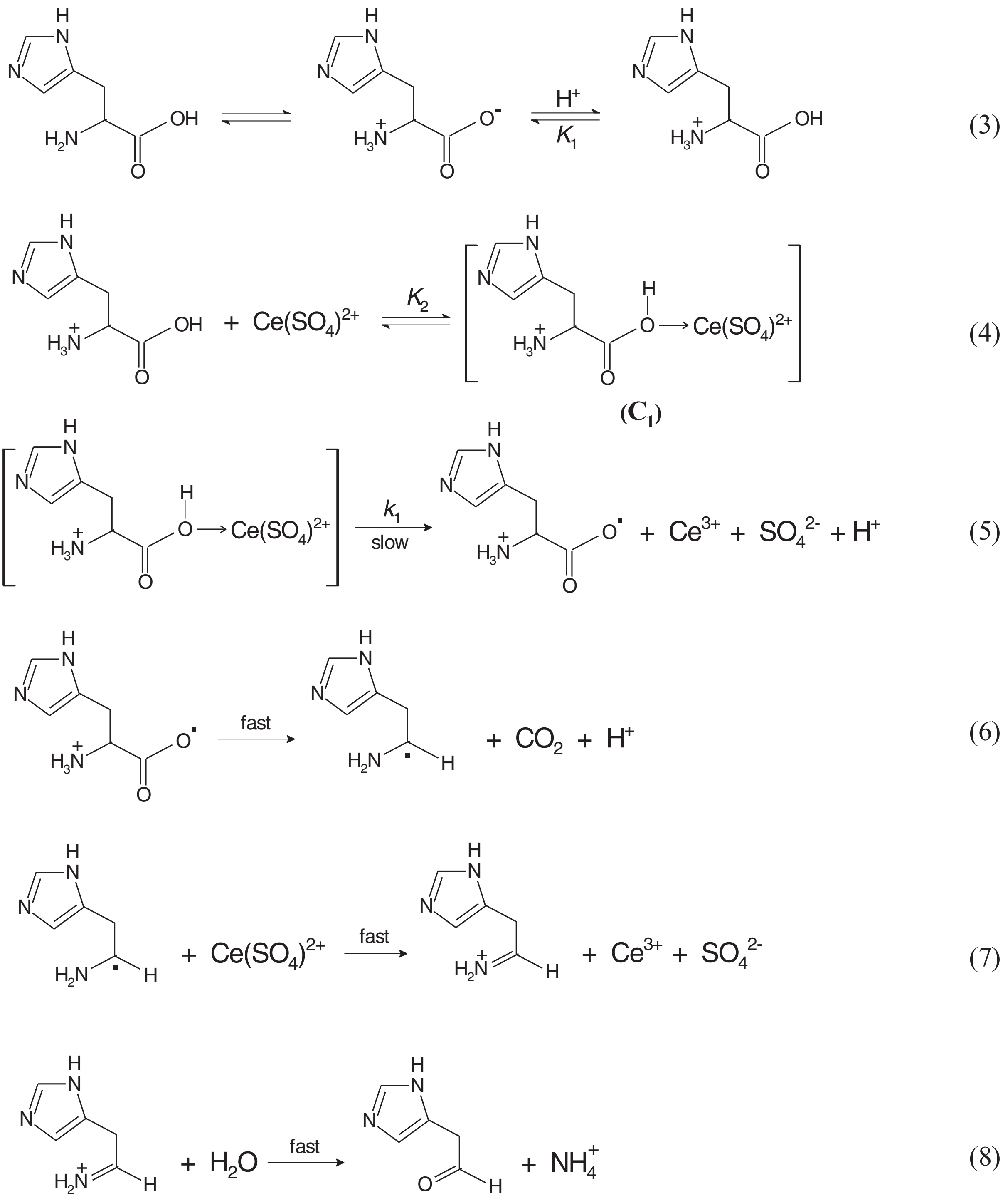
The oxidation reaction is proposed to be a one-electron process in the rate-determining step, which

Table II Activation Parameters of k' in the Uncatalyzed and Metal Ions–Catalyzed Oxidations of Histidine by Cerium(IV) in Sulfuric Acid Solutions. [His] = 6.0 × 10^{-3}, [Ce(IV)] = 2.0 × 10^{-4}, [H^+] = 2.0, I = 3.0, [Ag(I)] = 8.0 × 10^{-6}, and [Cu(II)] = 8.0 × 10^{-4} mol dm^{-3}

Reaction	$\Delta S^{\neq}$ (J $mol^{-1}K^{-1}$)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}{}_{298}$ (kJ mol^{-1})	$E_a{}^{\neq}$ (kJ mol^{-1})
Uncatalyzed reaction	−94.04	60.46	88.47	69.09
Ag(I)-catalyzed reaction	−54.42	27.21	43.43	36.36
Cu(II)-catalyzed reaction	−76.71	39.30	62.16	47.27

Experimental error ±3%.

$$CeSO_4^{2+} + HSO_4^- \overset{K}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \qquad (2)$$



Scheme 1 Mechanism of uncatalyzed oxidation of histidine by cerium(IV) in sulfuric acid solution.

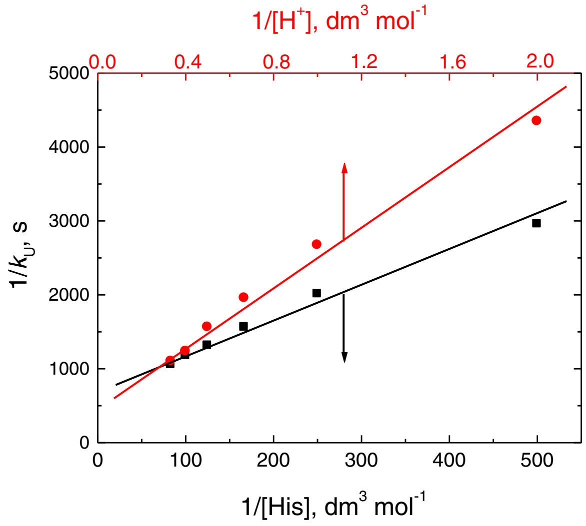


Figure 8 Plots of $1/k_U$ versus 1/[His] and 1/[H$^+$] for the uncatalyzed oxidation of histidine by cerium(IV) in sulfuric acid solution. [Ce(IV)] $= 2.0 \times 10^{-4}$ and $I = 3.0$ mol dm^{-3} at 25°C. [Color figure can be viewed at wileyonlinelibrary.com]

leads to decomposition of the intermediary complex forming an intermediary radical and Ce(III) ion. The formation of a free radical is evident through the acrylonitrile polymerization test. The rate was not affected by Ce(III), suggesting that the reaction step involving decomposition of the intermediary complex into a histidine free radical and Ce(III) ion may not be a reversible process. The rate-determining step should be irreversible, which is generally the case for one-electron oxidants [35]. Next, decarboxylation of the histidine free radical occurred, forming a new radical intermediary (X$^\bullet$). The latter was rapidly attacked by another Ce(SO$_4$)$^{2+}$ species to yield the final oxidation products. The suggested mechanism is illustrated in Scheme 1.

The suggested mechanism leads to the following rate-law expression (see the Appendix),

$$\text{Rate} = \frac{k_1 K_1 K_2[\text{Ce(IV)}][\text{His}][\text{H}^+]}{1 + K_1[\text{H}^+] + K_1 K_2[\text{His}][\text{H}^+] + K[\text{HSO}_4^-](K_1 + [\text{H}^+]^{-1})} \tag{9}$$

The rate law (9) is consistent with all the observed orders with respect to different species.

Under pseudo–first-order conditions, the rate law can be expressed by Eq. (10),

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = k_U\,[\text{Ce (IV)}] \tag{10}$$

Comparing Eqs. (9) and (10), we obtain

$$k_U = \frac{k_1 K_1 K_2[\text{His}][\text{H}^+]}{1 + K_1[\text{H}^+] + K_1 K_2[\text{His}][\text{H}^+] + K[\text{HSO}_4^-](K_1 + [\text{H}^+]^{-1})} \tag{11}$$

and with rearrangement of Eq. (11), Eqs. (12) and (13) are obtained:

$$\frac{1}{k_U} = \left(\frac{1 + K_1[\text{H}^+]}{k_1 K_1 K_2[\text{H}^+]}\right)\frac{1}{[\text{His}]} + \frac{1}{k_1} + K'K[\text{HSO}_4^-] \tag{12}$$

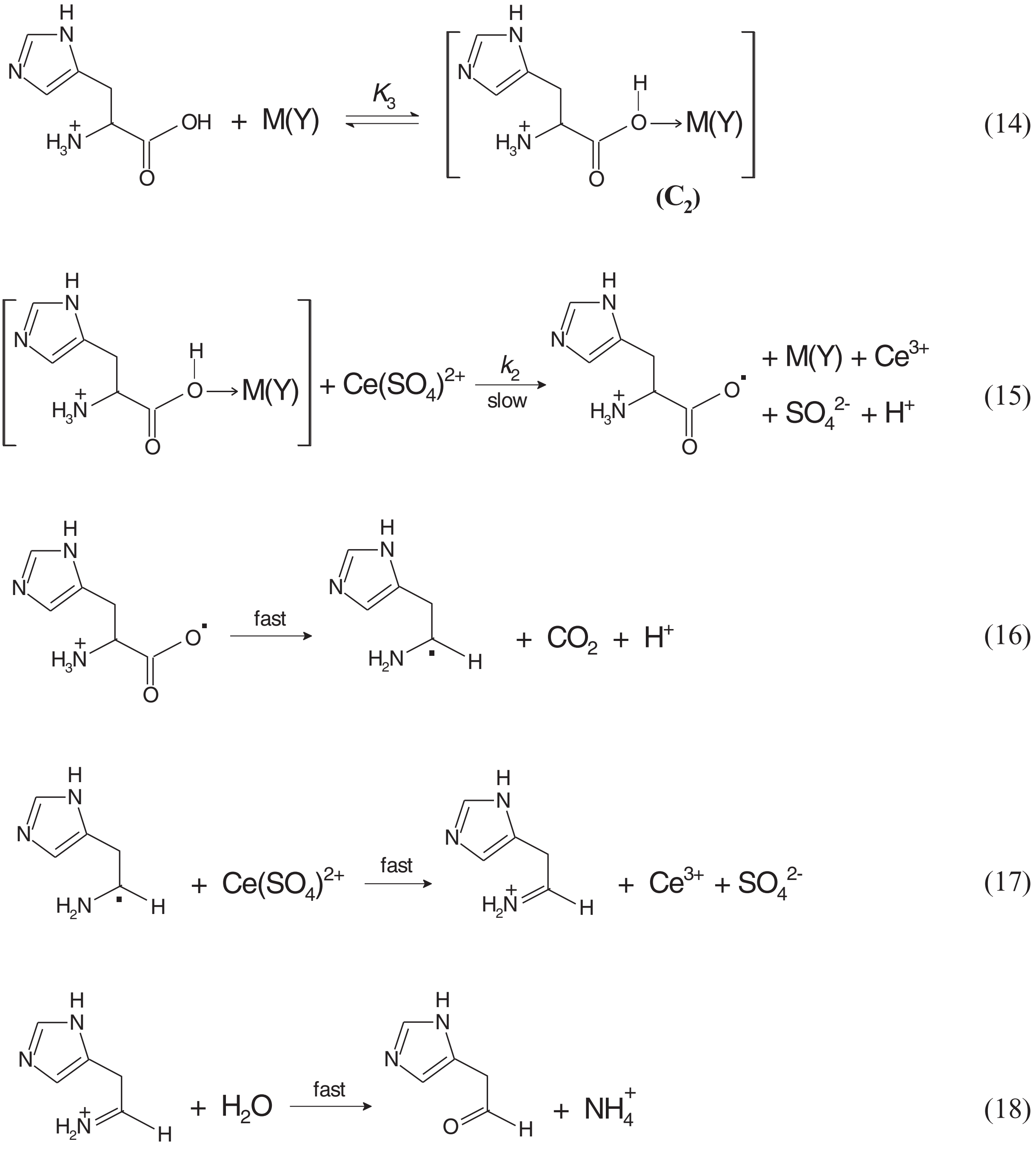
$$\frac{1}{k_U} = \left(\frac{1}{k_1 K_1 K_2[\text{His}]}\right)\frac{1}{[\text{H}^+]} + \frac{1}{k_1 K_2[\text{His}]} + \frac{1}{k_1} + K'K[\text{HSO}_4^-] \tag{13}$$

where $K' = \dfrac{K_1 + [\text{H}^+]}{k_1 K_1 K_2[\text{His}][\text{H}^+]}$

Regarding to Eqs. (12) and (13), the plots of $1/k_U$ versus 1/[His] at constant [H$^+$] and $1/k_U$ versus 1/[H$^+$] at constant [His] should be linear with positive intercepts and are found to be so as shown in Fig. 8.

Mechanism of Metal Ions–Catalyzed Oxidations

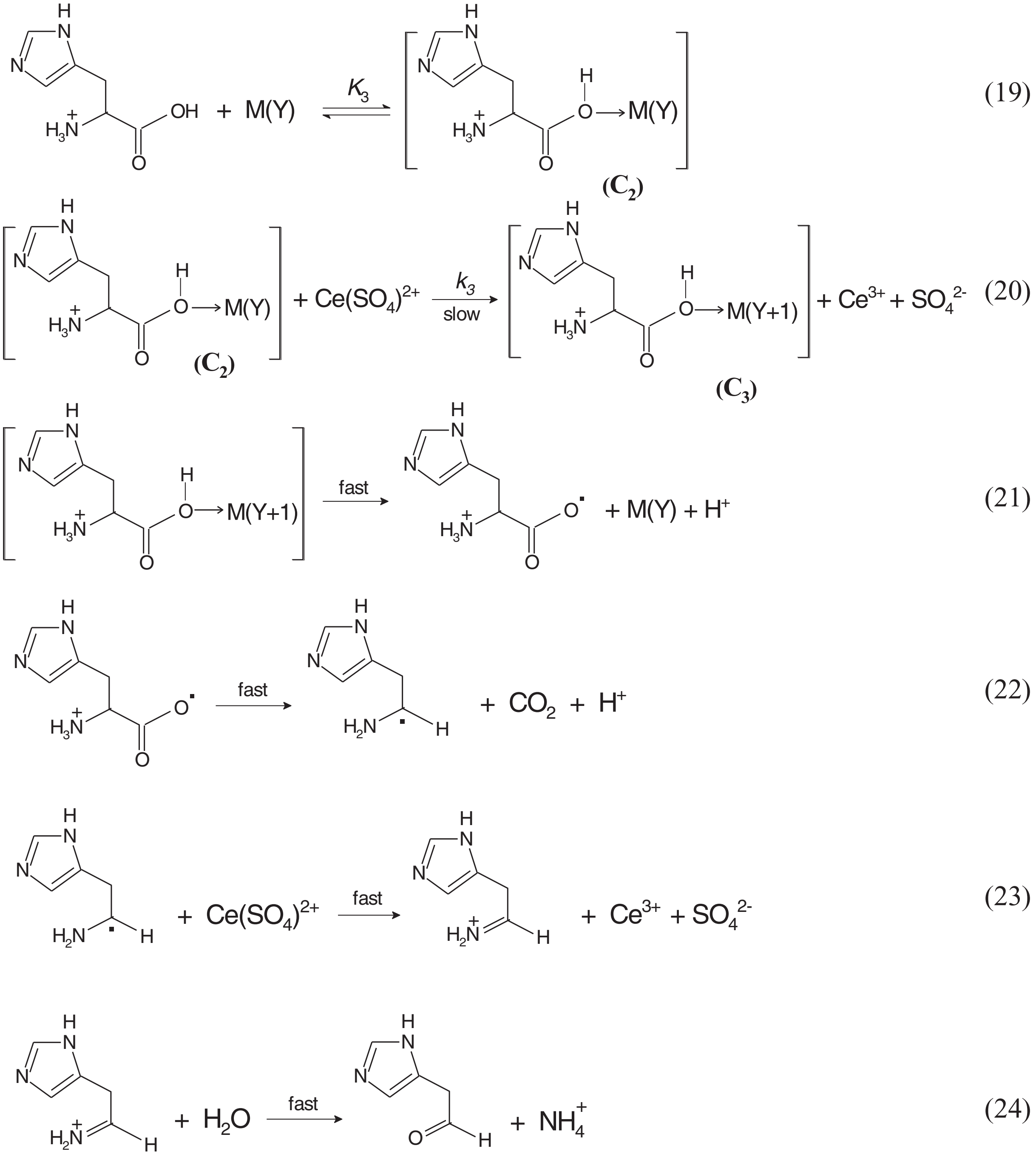
The kinetics of the oxidations of His by cerium(IV) in sulfuric acid solutions in the presence of small amounts of silver(I) and copper(II) catalysts are similar to that for the uncatalyzed oxidation reaction. In addition, these reactions show first order with respect to silver(I) and copper(II) concentrations. Less than unit orders for the concentrations of His and metal ion catalysts suggest formation of complexes between His and metal ions catalysts [3,12–14,36] prior to reaction with the oxidant. Complexes formation was also proved kinetically by the nonzero intercepts of the plots of [M(Y)]/k_C versus 1/[His] (M = metal; Y = oxidation state of M) (Fig. 9). Such complexes have earlier been reported between His and silver(I) [13] and between His and copper(II) [14]. These complexes react in slow steps with Ce(SO$_4$)$^{2+}$ to give rise to the intermediary radical and Ce(III) ion with regeneration of the catalyst. This is followed by decarboxylation of His free radical, forming a new radical intermediary (X$^\bullet$). The latter is rapidly attacked by another Ce(SO$_4$)$^{2+}$ species to yield the final oxidation products as illustrated in Scheme 2.



Scheme 2 Mechanism of metal ions-catalyzed oxidations of histidine by cerium(IV) in sulfuric acid solutions.

An alternative oxidation mechanism [3,12,36] for metal ions–catalyzed oxidations may be proposed. It involves formation of an intermediary complex between the metal ion catalyst, M(Y), and the amino acid (C_2), that on further interaction with Ce(IV) in the rate-determining step yields another complex (C_3) of a higher valence metal ion, M(Y+1), and Ce(III) ion. Such complex rapidly decomposes giving rise to the intermediary radical with regeneration of the catalyst M(Y), followed by subsequent fast steps to yield the final oxidation products as illustrated in Scheme 3.

In a similar manner to the uncatalyzed reaction, the proposed mechanism leads to the following



Scheme 3 An alternative mechanism of metal ions–catalyzed oxidations of histidine by cerium(IV) in sulfuric acid solutions.

rate law expression shown in the following equation:

$$\text{Rate} = \frac{k_2K_1K_3[\text{Ce(IV)}][\text{His}][\text{H}^+][\text{M(Y)}]}{1 + K_1[\text{H}^+] + K_1K_3[\text{His}][\text{H}^+] + K[\text{HSO}_4^-](K_1 + [\text{H}^+]^{-1})} \tag{25}$$

The rate law expressed in Eq. (25) is consistent with all the observed orders with respect to different species. Under pseudo–first-order conditions, the rate law can be expressed by Eq. (26),

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = k_\text{C}\,[\text{Ce (IV)}] \tag{26}$$

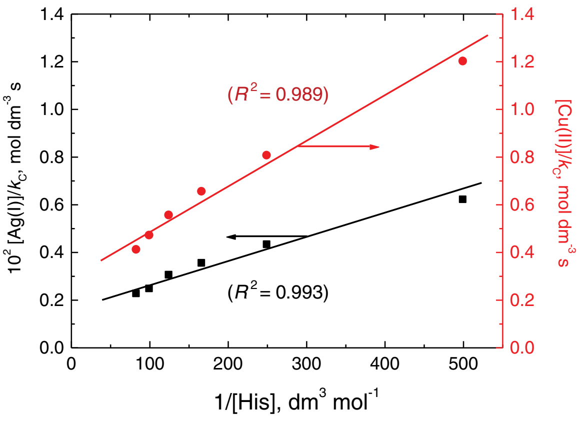


Figure 9 Plots of [Ag(I)]/k_C and [Cu(II)]/k_C versus 1/[His] in the metal ions–catalyzed oxidations of histidine (His) by cerium(IV) in sulfuric acid solutions. [Ce(IV)] = 2.0×10^{-4}, [H^+] = 2.0, and I = 3.0 mol dm^{-3} at 25°C. [Color figure can be viewed at wileyonlinelibrary.com]

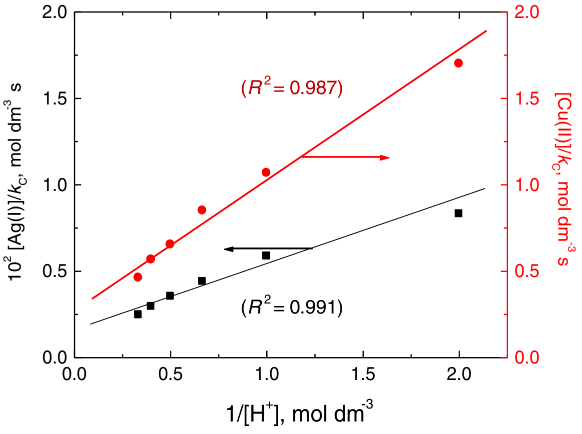


Figure 10 Plots of [Ag(I)]/k_C and [Cu(II)]/k_C versus 1/[H^+] in the metal ions–catalyzed oxidations of histidine (His) by cerium(IV) in sulfuric acid solutions. [His] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, and I = 3.0 mol dm^{-3} at 25°C. [Color figure can be viewed at wileyonlinelibrary.com]

Comparing Eqs. (25) and (26), we obtain Eq. (27),

$$k_C = \frac{k_2K_1K_3[\mathrm{His}][\mathrm{H}^+][\mathrm{M(Y)}]}{1 + K_1[\mathrm{H}^+] + K_1K_3[\mathrm{His}][\mathrm{H}^+] + K[\mathrm{HSO}_4^-](K_1 + [\mathrm{H}^+]^{-1})} \qquad (27)$$

With rearrangement of Eq. (27), the following two equations are obtained:

$$\frac{[\mathrm{M(Y)}]}{k_C} = \left(\frac{1 + K_1[\mathrm{H}^+]}{k_2K_1K_3[\mathrm{H}^+]}\right)\frac{1}{[\mathrm{His}]} + \frac{1}{k_2} + K'K[\mathrm{HSO}_4^-] \qquad (28)$$

$$\frac{[\mathrm{M(Y)}]}{k_C} = \left(\frac{1}{k_2K_1K_3[\mathrm{His}]}\right)\frac{1}{[\mathrm{H}^+]} + \frac{1}{k_2K_3[\mathrm{His}]} + \frac{1}{k_2} + K''K[\mathrm{HSO}_4^-] \qquad (29)$$

where $K'' = \dfrac{K_1 + [\mathrm{H}^+]^{-1}}{k_2K_1K_3[\mathrm{His}][\mathrm{H}^+]}$

According to Eqs. (28) and (29), plots of [M(Y)]/k_C versus 1/[His] at constant [H^+], and [M(Y)]/k_C against 1/[H^+] at constant [His], should be linear with positive intercepts on the [M(Y)]/k_C axes. The experimental results satisfy these requirements, as shown in Figs. 9 and 10, respectively.

The mechanism of catalysis by metal ions can be quite complicated due to formation of different intermediate complexes. Although the mechanism of catalysis depends on the nature of the substrate, oxidant, and the experimental conditions, it has been shown [14] that metal ions act as catalysts by a few different paths such as the formation of complexes with reactant, or direct oxidation of the substrate, or through the formation of free radicals.

CONCLUSIONS

A comparative study of the oxidations of histidine by cerium(IV) in aqueous sulfuric acid solutions in the absence and presence of silver(I) and copper(II) catalysts was performed. The oxidation reaction was found to occur with a slow rate in the absence of the catalysts. The catalytic efficiency of Ag(I) was higher than that of Cu(II). In both cases, the final oxidation products of histidine were identified as 2-imidazole acetaldehyde, ammonium ion, and carbon dioxide.

APPENDIX: DERIVATION OF RATE-LAW EXPRESSION OF THE UNCATALYZED OXIDATION REACTION

According to the proposed mechanistic Scheme 1,

$$\mathrm{Rate} = \frac{-d[\mathrm{Ce(IV)}]}{dt} = k_1\,[\mathrm{C}_1] \qquad (\mathrm{A1})$$

According to reactions (2)–(4),

$$K = \frac{[\mathrm{Ce(SO_4)_2}][\mathrm{H}^+]}{[\mathrm{Ce(SO_4)}^{2+}][\mathrm{HSO}_4^-]},\ \left[\mathrm{Ce\,(SO_4)}^{2+}\right] = \frac{[\mathrm{Ce(SO_4)_2}][\mathrm{H}^+]}{K[\mathrm{HSO}_4^-]} \qquad (\mathrm{A2})$$

$$K_1 = \frac{[\mathrm{His}^+]}{[\mathrm{His}][\mathrm{H}^+]},\ \left[\mathrm{His}^+\right] = K_1\,[\mathrm{His}]\left[\mathrm{H}^+\right] \quad \text{(A3)}$$

$$\begin{aligned} K_2 &= \frac{[\mathrm{C}_1]}{[\mathrm{Ce(SO_4)}^{2+}][\mathrm{His}^+]},\ [\mathrm{C}_1] \\ &= K_2\left[\mathrm{Ce\,(SO_4)}^{2+}\right][\mathrm{His}^+] \\ &= \frac{K_1K_2[\mathrm{Ce(SO_4)_2}][\mathrm{His}][\mathrm{H}^+]^2}{K[\mathrm{HSO_4^-}]} \end{aligned} \quad \text{(A4)}$$

Substituting Eq. (A4) into Eq. (A1) leads to Eq. (A5).

$$\text{Rate} = \frac{k_1K_1K_2[\mathrm{Ce(SO_4)_2}][\mathrm{His}][\mathrm{H}^+]^2}{K[\mathrm{HSO_4^-}]} \quad \text{(A5)}$$

The total concentration of histidine is given as follows:

$$[\mathrm{His}]_\mathrm{T} = [\mathrm{His}]_\mathrm{F} + \left[\mathrm{His}^+\right] + [\mathrm{C}_1] \quad \text{(A6)}$$

$$[\mathrm{His}]_\mathrm{F} = \frac{[\mathrm{His}]_\mathrm{T}}{1 + K_1[\mathrm{H}^+] + \frac{K_1K_2[\mathrm{Ce(SO_4)_2}][\mathrm{H}^+]^2}{K[\mathrm{HSO_4^-}]}} \quad \text{(A7)}$$

In view of low $\mathrm{Ce(SO_4)_2}$ concentration used,

$$[\mathrm{His}]_\mathrm{F} = \frac{[\mathrm{His}]_\mathrm{T}}{1 + K_1[\mathrm{H}^+]} \quad \text{(A8)}$$

Also,

$$[\mathrm{Ce\,(IV)}]_\mathrm{T} = [\mathrm{Ce\,(SO_4)}^{2+}] + \left[\mathrm{Ce\,(SO_4)_2}\right] + [\mathrm{C}_1] \quad \text{(A9)}$$

$$\left[\mathrm{Ce\,(SO_4)_2}\right]_\mathrm{F} = \frac{[\mathrm{Ce(IV)}]_\mathrm{T}K[\mathrm{HSO_4^-}]}{[\mathrm{H}^+] + K[\mathrm{HSO_4^-}] + K_1K_2[\mathrm{His}][\mathrm{H}^+]^2} \quad \text{(A10)}$$

Substituting Eqs. (A8) and (A10) into Eq. (A4) leads to Eq. (A11),

$$\text{Rate} = \frac{k_1K_1K_2[\mathrm{Ce(IV)}][\mathrm{His}][\mathrm{H}^+]^2}{[\mathrm{H}^+] + K_1[\mathrm{H}^+]^2 + K_1K_2[\mathrm{His}][\mathrm{H}^+]^2 + K_1^2K_2[\mathrm{His}][\mathrm{H}^+]^3 + K[\mathrm{HSO_4^-}] + KK_1[\mathrm{HSO_4^-}][\mathrm{H}^+]} \quad \text{(A11)}$$

For low histidine concentration,

$$\text{Rate} = \frac{k_1K_1K_2[\mathrm{Ce(IV)}][\mathrm{His}][\mathrm{H}^+]}{1 + K_1[\mathrm{H}^+] + K_1K_2[\mathrm{His}][\mathrm{H}^+] + K[\mathrm{HSO_4^-}](K_1 + [\mathrm{H}^+]^{-1})} \quad \text{(A12)}$$

Under pseudo–first-order conditions,

$$\text{Rate} = \frac{-d[\mathrm{Ce(IV)}]}{dt} = k_\mathrm{U}\,[\mathrm{Ce\,(IV)}] \quad \text{(A13)}$$

Comparing Eqs. (A12) and (A13), we obtain Eq. (A14),

$$k_\mathrm{U} = \frac{k_1K_1K_2[\mathrm{His}][\mathrm{H}^+]}{1 + K_1[\mathrm{H}^+] + K_1K_2[\mathrm{His}][\mathrm{H}^+] + K[\mathrm{HSO_4^-}](K_1 + [\mathrm{H}^+]^{-1})} \quad \text{(A14)}$$

$$\frac{1}{k_\mathrm{U}} = \left(\frac{1 + K_1[\mathrm{H}^+]}{k_1K_1K_2[\mathrm{H}^+]}\right)\frac{1}{[\mathrm{His}]} + \frac{1}{k_1} + K'K[\mathrm{HSO_4^-}] \quad \text{(A15)}$$

$$\begin{aligned} \frac{1}{k_\mathrm{U}} &= \left(\frac{1}{k_1K_1K_2[\mathrm{His}]}\right)\frac{1}{[\mathrm{H}^+]} + \frac{1}{k_1K_2[\mathrm{His}]} \\ &\quad + \frac{1}{k_1} + K'K[\mathrm{HSO_4^-}] \end{aligned} \quad \text{(A16)}$$

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