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Role of surfactants on Fe(II) catalyzed L-tryptophan oxidation by persulfate

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The present study aims to explore the kinetics of Fe(II) catalyzed L-tryptophan (Trp) oxidation in micellar media by persulfate ion ($S_2O_8^{2-}$). The reaction's progress has been analyzed as an indicator of [$S_2O_8^{2-}$], temperature, [Trp], [Fe(II)], [Surfactant], ionic strength, and [H^+]. The $S_2O_8^{2-}$ undergoes a 1:1 stoichiometric interaction with Trp. The observed reaction exhibits first-order kinetics with regards to [$S_2O_8^{2-}$], fractional-first-order with respect to [H^+], linear reliance to [Fe(II)], and invariance with respect to [Trp] within the range of concentrations investigated. The observed decrement in reaction rate upon electrolyte introduction is suggestive of a negative salt effect. The oxidation rate is significantly enhanced by Fe(II) solution (as a catalyst) at lower concentrations. Both the cationic cetyltrimethylammonium bromide (CTAB) and the anionic sodium dodecyl sulfate (SDS) have been shown to inhibit the oxidation rate, while the non-ionic Triton X-100 (TX-100) does not have a noticeable impact on the reaction rate.

Keywords: Surfactant, Micelle encapsulation, Oxidation, Persulfate, Iron(II) catalyzed, L- Tryptophan

One of the most fascinating areas in organic chemistry is the study of amino acids. The biosynthesis of polypeptides, proteins, and nucleotides are only a few of the metabolic processes in which they play a key role[1-5]. In order to better comprehend certain facets of enzyme kinetics, it may be necessary to conduct extensive research on the mechanism of related nonenzymatic chemical procedures in amino acid oxidation[6-10]. Under various experimental setups, amino acids have been oxidized by a range of reagents, and they frequently go through deamination and oxidative decarboxylation[11]. However, the different reaction systems may proceed *via* distinct mechanisms. The oxidation of amino acids is exceptionally interesting since different oxidants result in diverse oxidation products. Tryptophan, an essential amino acid found abundantly in protein-rich diets, has been employed therapeutically for the management of insomnia and sleep disorders, as well as for enhancing mood[12,13]. Upon ingestion, tryptophan undergoes metabolic processes leading to the synthesis of various bioactive metabolites, such as serotonin and melatonin[14].

The persulfate ion exhibits remarkable oxidizing capabilities in aqueous solution, making it one of the most potent oxidizing agents[15-20]. The reaction: $2SO_4^-(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$ is thought to have a typical oxidation-reduction potential of -2.01 volts[20]. Reactions including this particular ion, nevertheless, typically exhibit sluggish kinetics at ambient temperatures. Numerous investigations have been conducted to study the kinetic aspects of various persulfate oxidations. Despite the favorable standard free energy change, persulfate oxidation of numerous reducing agents at 25°C requires a catalyst[20]. The Ag(I) catalyst has been examined the most, while Fe(II), and Cu(II) reactions were also investigated[21-25]. Studies on persulfate oxidation have been discovered to be vital in synthetic[26,27], spectroscopy[28], and thermodynamic aspects[29,30]. The amino acid oxidation by persulfate has not garnered much attention despite the fact that it has been significantly employed to oxidize both organic and inorganic moieties[31,32]. The application of persulfate as an oxidizing agent is ascribed to its notable stability throughout a broad spectrum of *p*H values[20].

Surfactants' surface-active characteristics make them popular in modern businesses[33-35]. Surfactants' amphiphilic structure-hydrophilic head and hydrophobic tail give them surface action[36]. At lower concentrations, the behavior of surfactant molecules resembles that of typical solutes. However, once a specific concentration is reached, these molecules aggregate to form micelles. This concentration, at which the process of micellization initiates, is referred to as the critical micelle concentration (CMC)[37]. The primary factor driving the aggregation of surfactant molecules is the hydrophobic interaction that occurs between the hydrocarbon chains. Instead of combining to produce a continuous phase, the micelles form a micellar pseudo-phase by being evenly distributed throughout the aqueous medium. Micelles and surfactant solute molecules convert in milliseconds, reversibly. Thus, lowering the surfactant concentration below the CMC destroys the micelles and produces the original simple solution of surfactants. Micelle-bound reactants undergo a fundamentally different reaction environment when compared to pure solvents[33]. The reaction rate in a micellar medium is determined by the extent of interaction between the substrate and the micelle aggregates. The redox processes that take place within micellar systems can be regarded as useful models for gaining a deeper understanding of the electron transport mechanisms that are prevalent in biological systems[38-41].

This study investigates the impact of cationic, anionic, and neutral surfactants on the oxidation rate of Trp by acidic persulfate in the presence of Fe(II) metal ions as a catalyst. The oxidation rate of amino acids by persulfate exhibits a relatively sluggish pace. Thus, the rate enhancement is indeed challenging. The previous literature has already documented the enhancement of amino acid oxidation by persulfate in the presence of a metal catalyst[32,42]. Several researchers have documented the metal-catalyzed oxidation of organic moieties in a surfactant medium using persulfate[43,44]. However, the effect of surfactants on metal-catalyzed oxidation of amino acid by persulfate has never been reported.

Materials and Methods

Reagents Used

The kinetic experiment was conducted using double-deionized water and analytical-grade reagents over the entire study. Surfactants utilized, cetyltrimethylammonium bromide (CTAB) (AR, Fisher Scientific, India), sodium dodecyl sulfate (SDS) (AR, Fisher Scientific, India), and TX-100 (AR, Fisher Scientific, India) were of utmost purity. Himedia India, supplied L-tryptophan (99%), $K_2S_2O_8$ (99.9%), and $FeSO_4.5H_2O$ (99.5%) which was utilized without subsequent purification. Na_2SO_4 (Molechem) controlled ionic strength, while HCl (Merck, India) regulated the *p*H of the reaction mixture.

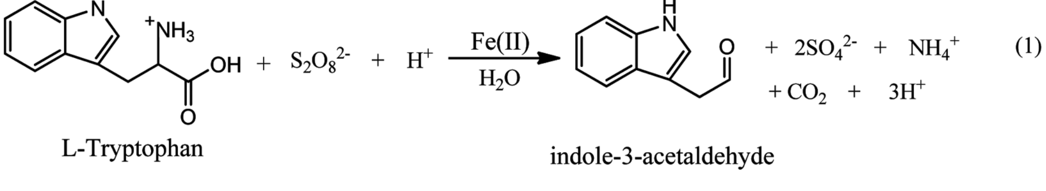
Kinetic Measurements

Following thermal equilibration at 303 K for 30 min, all of the reactive solutions were quickly mixed in succession: Trp, surfactant, HCl, Na_2SO_4, Fe(II), and $K_2S_2O_8$. The advancement of the chemical reaction was observed by employing iodometric analysis to quantify the unreacted persulfate at various time intervals[45]. The first-order rate constant (k_f) was calculated using a non-linear least squares fitting approach to a graph plotted between logarithms of persulfate concentration *versus* time.

Results and Discussion

The measured quantities of $K_2S_2O_8$ were permitted to undergo a reaction with a surplus of ten times the amount of Trp in the presence of 3.0×10^{-3} M H^+ ions and a fixed quantity of Fe(II) at a temperature of 303 K within a sealed container until the reaction reached its conclusion. Through iodometric analysis, the concentration of unreacted $S_2O_8^{2-}$ was determined. The experimental findings indicate that Trp and $S_2O_8^{2-}$ undergo a chemical reaction with a stoichiometric ratio of 1:1, as represented by equation 1 (Scheme 1).

To evaluate the participation of free radicals in the oxidation mechanism, a polymerization assay has been conducted. With defined amounts of acrylonitrile scavenger, reaction mixtures are kept inert for six hours. The formation of white precipitates upon dilution with methanol demonstrates the involvement of free radicals in this process. These



Scheme 1 — Fe^{2+} catalysed oxidation of L-Tryptophan by $S_2O_8^{2-}$

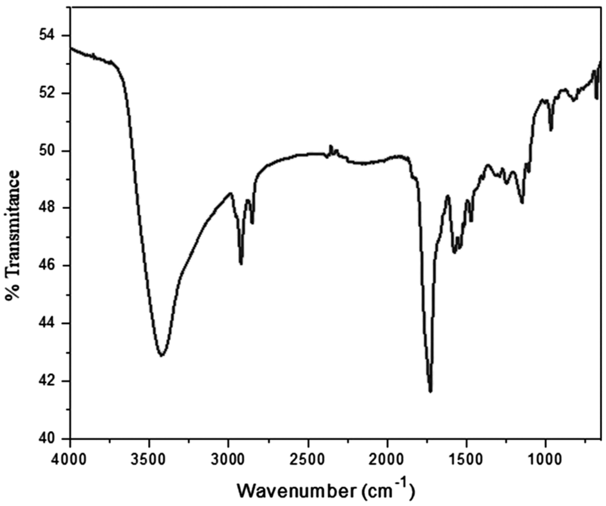


Fig. 1 — FTIR spectrum of the ultimate product (indole-3-acetaldehyde)

studies failed in the defection of $S_2O_8^{2-}$ under comparable circumstances, suggesting the participation of $S_2O_8^{2-}$ in the generation of free radicals.

The oxidation product of Trp is identified through thin-layer chromatography as indole-3-acetaldehyde, which is characterized by the formation of its 2,4-DNP derivative. The presence of a singular peak on the chromatogram is indicative of the formation of a solitary product. The production of indole-3-acetaldehyde has been confirmed by prior investigations utilizing diverse oxidizing agents to oxidize amino acids[46,47].

Absorption peaks can be seen in the FTIR spectra of the ultimate product, indole-3-acetaldehyde, at 1730 cm^{-1}, 1610-1520 cm^{-1}, 3426 cm^{-1}, and 2750-2950 cm^{-1}. These spectral features can be attributed to the stretching vibrations of the C=O bond, C=C bond, N-H bond and the C-H bond of the CHO group, respectively (Fig. 1). C, 75.74; O, 10.11; N; 8.52; and H, 5.63; from an elemental analysis also corroborated the production of indole-3-acetaldehyde.

Impact of variation of [Surfactant] on oxidation rate

Surfactants possess the ability to modulate the rate of chemical reactions while also promoting the uniform dispersion of organic reactants within an aquatic environment, contingent on the charges they carry (neutral, cationic, and anionic)[43]. The advancement in reaction rate can be ascribed to the formation of micelles by the surfactants above their CMC, as well as the gathering of reactants through induced dipole-induced dipole, dipole-induced dipole, or ion-dipole interactions within a confined region (stern layer) surrounding the micelle. In the context of SDS and CTAB, it has been duly noted that the oxidation rate of Trp experiences a significant decrease as the concentration of surfactants increases, and this reduction persists even in the presence of Fe(II). In the scenario of TX-100, the observed oxidation rate did not exhibit any substantial alteration. Furthermore, TX-100, despite the presence of Fe(II), exhibits an inability to synergistically augment the reaction rate, potentially attributed to its non-ionic properties (Table 1).

Impact of variation of [H$^+$] on oxidation rate

Previous investigations on the oxidation of organic moieties, both catalyzed and unanalyzed, involving $S_2O_8^{2-}$, have elucidated the significance of [H$^+$] in governing the rate of oxidation[35-37]. The investigation focused on exploring the reaction rate within [H$^+$] spanning from $1.0{\times}10^{-3}$ M to $6.0{\times}10^{-3}$ M by calculating the first order rate constant under different [H$^+$].

Fig. 2 illustrates a positive intercepted linear correlation between [H$^+$] and k_f, indicating that the reaction follows a fractional-first-order kinetics with respect to [H$^+$]. At low [H$^+$], the reaction rate is modest, followed by a precise increase in accordance with [H$^+$] within the examined range. Amino acids are believed to exist as zwitterions and exhibit a propensity for protonation in acidic conditions[48]. $S_2O_8^{2-}$ also predominantly manifests in its protonated state ($HS_2O_8^-$) in an acidic medium[29]. The reactants' protonated species can be regarded as the more reactive entities that predominantly govern the reaction kinetics[49]. The presence of a protonated state of $S_2O_8^{2-}$ and Trp is hypothesized to be responsible for the increased reaction observed in an aqueous solution with increment in [H$^+$].

Impact of variation of [Trp] on oxidation rate

At the designated [H$^+$] concentration, the effect of [Trp] on the rate of oxidation was studied at a temperature of 303 K within the 1.0×10^{-2} M to 6.0×10^{-2} M concentration interval. Based on the determined k_f value for every Trp (Table 2), it can be observed that the [Trp] range being studied demonstrates zero-order kinetics since the overall reaction order remains constant at one when the reactants are present in equimolecular concentrations.

Table 1 — Effect of variation of [Surfactant] on first order rate constant (k_f)

Experimental Conditions: $[S_2O_8^{2-}] = 3.0 \times 10^{-2}$ M, I = 0.25 M (Na_2SO_4), $[H^+] = 3.0 \times 10^{-3}$ M, Temp = 303 K ± 0.1 K, $[Fe(II)] = 5.0 \times 10^{-5}$ M, and $[Trp] = 3.0 \times 10^{-2}$ M

$Fe(II) \times 10^5$, M	Micellar Catalyst, M		$k_f \times 10^4$, s^{-1}
0.0	None		4.36 ± 0.07
5.0	None		6.54 ± 0.34
5.0	SDS	0.005	6.09 ± 0.19
		0.01	5.71 ± 0.20
		0.02	4.68 ± 0.13
		0.03	4.09 ± 0.07
		0.04	3.35 ± 0.11
		0.06	2.84 ± 0.12
		0.08	2.37 ± 0.09
		0.1	1.92 ± 0.14
		0.12	1.47 ± 0.07
5.0	CTAB	0.005	5.28 ± 0.21
		0.01	4.63 ± 0.18
		0.02	3.81 ± 0.16
		0.03	3.12 ± 0.19
		0.04	2.24 ± 0.09
		0.06	1.73 ± 0.10
		0.08	1.22 ± 0.08
5.0	TX-100	0.0005	6.68 ± 0.28
		0.001	6.62 ± 0.30
		0.002	6.53 ± 0.26
		0.003	6.42 ± 0.35
		0.004	6.57 ± 0.31
		0.006	6.49 ± 0.24
		0.008	6.60 ± 0.21

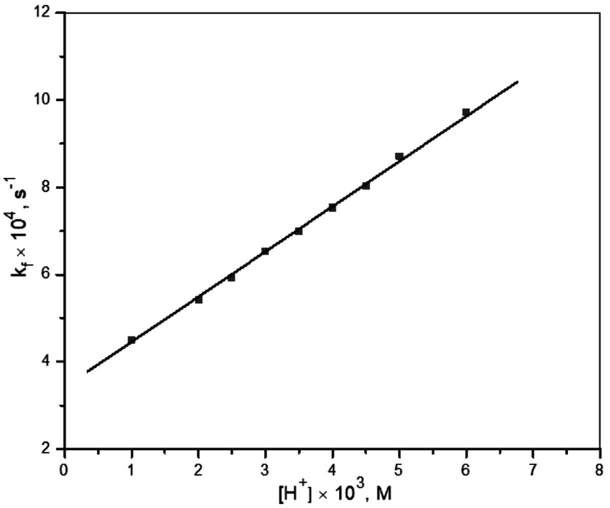


Fig. 2 — Effect of variation of $[H^+]$ on rate constant (k_f) at $[S_2O_8^{2-}] = 3.0 \times 10^{-2}$ M, I = 0.25 M (Na_2SO_4), Temp = 303 K ± 0.1 K, $[Fe(II)] = 5.0 \times 10^{-5}$ M, and $[Trp] = 3.0 \times 10^{-2}$ M

Impact of variation of $[S_2O_8^{2-}]$ on oxidation rate

Under the ideal circumstances of $[H^+]$ and [Trp], while keeping the remaining reaction variables unchanged, the rate constant was determined as an indicator of $S_2O_8^{2-}$ in the concentration ranging from 1.0×10^{-2} M to 6.0×10^{-2} M. The apparent relationship between the plot of k_f against $[S_2O_8^{2-}]$ (Fig. 3) exhibited a linear correlation having zero intercepts. The experimental findings indicate that the $S_2O_8^{2-}$ dependencies exhibit first-order kinetics in aqueous surroundings.

Table 2 — Effect of variation of [Trp] on first order rate constant (k_f)

Experimental Conditions: $[S_2O_8^{2-}] = 3.0 \times 10^{-2}$ M, I = 0.25 M (Na_2SO_4), $[H^+] = 3.0 \times 10^{-3}$ M, Temp = 303 K ± 0.1 K, and $[Fe(II)] = 5.0 \times 10^{-5}$ M

$[Trp] \times 10^2$ M	$k_f \times 10^4$, s^{-1}
1.0	6.68 ± 0.35
1.5	6.51 ± 0.28
2.0	6.46 ± 0.25
2.5	6.70 ± 0.36
3.0	6.54 ± 0.34
4.4	6.67 ± 0.23
5.0	6.43 ± 0.18
6.0	6.59 ± 0.31

Impact of variation of [Electrolyte] on oxidation rate

In order to investigate the effect of ionic strength on the rate of reaction, the concentrations of a neutral electrolyte (Na_2SO_4) were varied within the range of 0.1 to 0.5 M. The remaining process parameters were maintained constant at $[S_2O_8^{2-}] = 3.0\times10^{-2}$ M, $[H^+] = 3.0\times10^{-3}$ M, Temp = 303 K ± 0.1 K, [Fe(II)] = 5.0×10^{-5} M, and [Trp] = 3.0×10^{-2} M. The observed trend of k_f with respect to ionic strength (I) displayed a negative salt effect, as depicted in Fig. 4. The decrement in oxidation rate with ionic strength supports the participation of oppositely charged Fe^{2+} and $HS_2O_8^-$ in the rate-determining step.

Impact of variation of [Fe(II)] on oxidation rate

It is of the utmost importance to investigate how [Fe(II)] affects the rate of reaction since Fe(II) facilitated oxidation reactions will eventually serve to quantify Fe(II) at a micro level. The first-order-rate constant (k_f) was computed by mixing the reactants under carefully optimized reaction conditions while altering the concentration of Fe(II). The observed correlation between the concentration of Fe(II) and k_f, as depicted in Fig. 5, depicts a linear relationship between the reaction rate and [Fe(II)] over the range of concentrations investigated. Since the linear trajectory does not intersect the origin, it is apparent that the uncatalyzed oxidation of Trp by $S_2O_8^{2-}$ is also feasible.

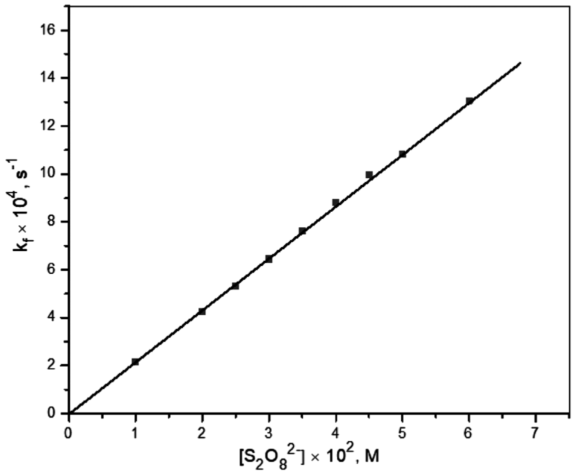


Fig. 3 — Effect of variation of $[S_2O_8^{2-}]$ on rate constant (k_f) at I = 0.25 M (Na_2SO_4), $[H^+] = 3.0\times10^{-3}$ M, Temp = 303 K ± 0.1 K, [Fe(II)] = 5.0×10^{-5} M, and [Trp] = 3.0×10^{-2} M

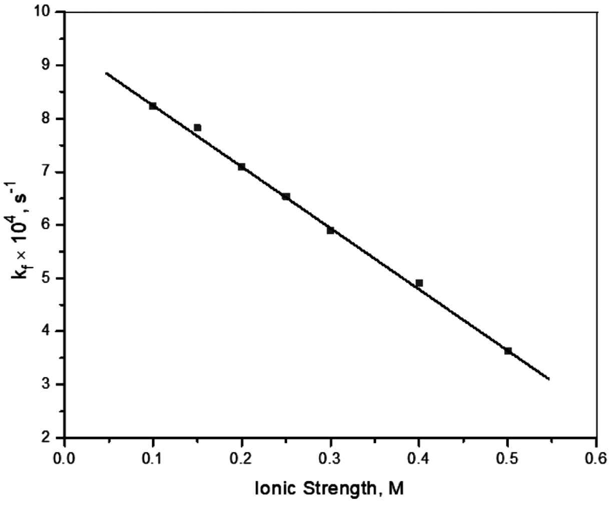


Fig. 4 — Effect of variation of [Electrolyte] on rate constant (k_f) at $[S_2O_8^{2-}] = 3.0\times10^{-2}$ M, $[H^+] = 3.0\times10^{-3}$ M, Temp = 303 K ± 0.1 K, [Fe(II)] = 5.0×10^{-5} M, and [Trp] = 3.0×10^{-2} M

Impact of temperature variation on oxidation rate

As anticipated, the oxidation rate is augmented under the optimum reaction conditions with the increases in temperature from 293 to 323 K. The kinetic investigation was deemed unsuitable at a significantly elevated temperature due to the end reaction product's propensity to degrade and the exceedingly fast reaction rate. The selection of 303 K as the temperature for the kinetic investigation was made due to the favorable occurrence of the reaction at a moderate rate at this particular temperature. Employing the Arrhenius equations the calculated activation energy (E_a), and enthalpy of activation ($\Delta H^{\#}$) values are 39.71 ± 2.07 k J $mole^{-1}$ and 37.19 ± 1.82 k J $mole^{-1}$ in an aqueous environment.

Mechanism

Fe(II) has demonstrated its efficacy as a catalyst in numerous redox reactions conducted in acidic and

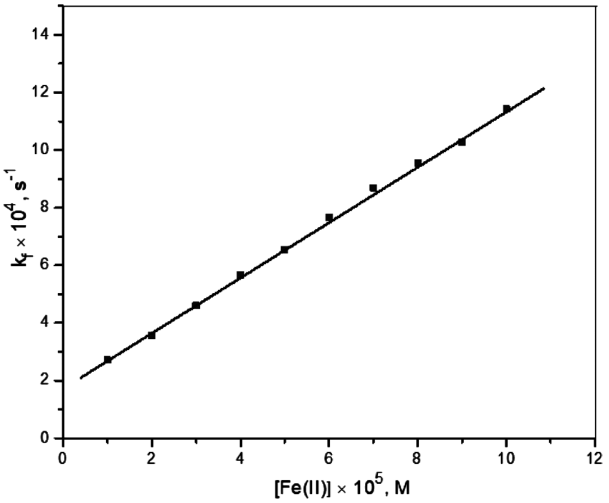
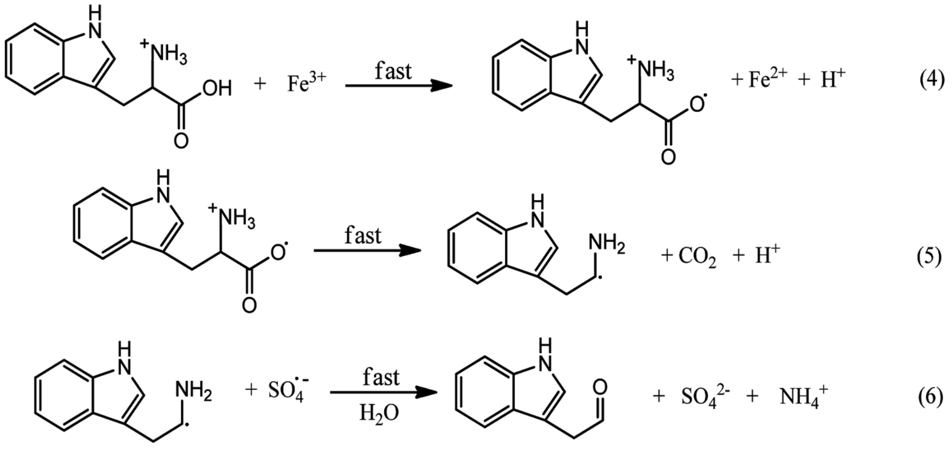


Fig. 5 — Effect of added [Fe(II)] on rate constant (k_f) at $[S_2O_8^{2-}] = 3.0\times10^{-2}$ M, I = 0.25 M (Na_2SO_4), $[H^+] = 3.0\times10^{-3}$ M, Temp = 303 K ± 0.1 K, and [Trp] = 3.0×10^{-2} M

$$S_2O_8^{2-} + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HS_2O_8^- \quad (2)$$

$$HS_2O_8^- + Fe^{2+} \xrightarrow[\text{slow}]{k} Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -} + H^+ \quad (3)$$



Scheme 2 — Probable mechanism of Fe^{2+} catalysed oxidation of L-Tryptophan by $S_2O_8^{2-}$

alkaline conditions. The oxidation of Trp by $S_2O_8^{2-}$ *via* Fe(II) catalysis was elucidated through a comprehensive analysis of the kinetic investigation and relevant literature[42-44]. The proposed mechanism, as depicted in Equations (2)-(6), represents the most probable pathway for this chemical transformation (Scheme 2).

Based on the observations, the Fe(II) catalyzed oxidation of amino acids by $S_2O_8^{2-}$ in an acidic environment proceeds through a series of intricate steps, progressing through the creation of protonated species of $S_2O_8^{2-}$. In the subsequent step (rate determining step), the $HS_2O_8^-$ oxidizes Fe^{2+} to Fe^{3+}, while $S_2O_8^{2-}$ undergoes reduction resulting in the formation of sulfate ion, and sulfate radical ion. The Fe^{3+} thus formed reacts with Trp^+ to produce Trp radical cation with the regeneration of Fe^{2+}. The Trp radical cation undergoes rapid decarboxylation, resulting in the formation of the corresponding amine free radical. The resultant free radical promptly reacts with sulfate radical ion, subsequently leading to hydrolysis and yielding the ultimate product (indole-3-acetaldehyde).

The most sluggish step in the provided scheme, Eq. (3), is regarded as the step that determines the rate.

$$\text{Reaction Rate} = -\frac{d[S_2O_8^{2-}]}{dt} = k\,[HS_2O_8^-] \quad \ldots (7)$$

Eq. 8 reflects the overall $[S_2O_8^{2-}]$.

$$[S_2O_8^{2-}]_T = [S_2O_8^{2-}]_F + [HS_2O_8^-] \quad \ldots (8)$$

Using equations 2, and 8 we get:

$$[HS_2O_8^-]_F = \frac{K_1[S_2O_8^{2-}]_T\,[H^+]}{1 + K_1\,[H^+]} \quad \ldots (9)$$

Using equations 7, and 9 we get:

$$\text{Reaction Rate} = -\frac{d[S_2O_8^{2-}]}{dt} = \frac{k\,K_1[S_2O_8^{2-}]_T\,[H^+][Fe^{2+}]}{1 + K_1\,[H^+]} \quad \ldots (10)$$

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

The rates of chemical reactions within a micellar medium are modulated by the distribution of reactants within the aqueous and micellar pseudophases, leading to either suppression or acceleration of these rates due to their inherent differences[50-53]. Interactions between reacting moieties and surfactant agglomerates, both hydrophobic and electrostatic in nature, along with the accompanying structural modifications in water molecules, affect the reaction rate. The monomeric surfactant exhibits catalytic properties when present at concentrations less than the CMC, thereby enhancing the pace of the reaction. Catalytic micelles arise from the accumulation of monomeric surfactants and substrate molecules, thereby expediting the reaction kinetics. The presence of premicellar regions exerts a significant influence on the kinetics of surfactant-mediated reactions[54,55]. The substrate within micellar aggregates exhibits reduced reactivity compared to that within premicellar complexes. Following the attainment of the CMC, the premicellar complexes undergo disintegration, leading to the formation of micelles[56]. This process effectively sustains the reaction rate.

The surfactant exhibits remarkable proficiency in generating micelles at the nano-scale and facilitating the convergence of all participating entities within the micellar medium. Micelles catalyze the reaction when both reactants are bound to the surfactant micelle, resulting in a rise in effective concentration. Moreover, the phenomenon of suppression occurs when one of the reactants is partitioned into the surfactant phase, while the remaining residue is present in the bulk solution. SDS, an anionic surfactant, undergoes micellization, resulting in the formation of a micelle characterized by a negatively charged periphery. Hence, it is imperative that anionic entities ($HS_2O_8^-$) be prohibited from accessing the micellar interface and the substrate within the stern layer[57]. The inhibitory action of SDS can be elucidated by the phenomenon in which SDS attracts Trp^+ ions, forcing $HS_2O_8^-$ ions to remain dispersed throughout the solution. Consequently, this leads to a decrease in the likelihood of the two reactants encountering one other. In the context of CTAB micelles, the scenario is entirely distinct. CTAB undergoes micellization, resulting in the formation of a micelle with a positively charged exterior. Hence, as a consequence of the electrostatic repulsion between the cationic surface and the H^+ and Trp^+ ions, the oxidation rate is attenuated, despite the existence of Fe(II) as a catalyst. In the instance of TX-100, the oxidation rate remains constant regardless of the concentration of TX-100. This is due to the non-ionic properties of the TX-100 micellar surface, which prevents it from attracting reactants to the micellar phase.

Conclusion

The current research adds to our understanding of the metal-catalyzed oxidation of amino acids by $S_2O_8^{2-}$ in a micellar milieu. Within the investigated range of $[S_2O_8^{2-}]$, the observed reaction exhibits first-order kinetics. The first-order-rate constant was found to be invariant to the [Trp] under investigation. The investigated reaction demonstrates a linear reliance on the [Fe(II)]. The observed decrement in reaction rate upon the addition of the electrolyte indicates a negative salt effect. H^+ plays a significant role in the reaction and exhibits fractional-first-order kinetics with regard to $[H^+]$. Surfactants, remarkable chemical entities, modulate the speed of various reactions. Metals, in conjunction with surfactants, have been utilized for decades to accelerate the rate of synthetic organic processes. In Trp oxidation by $S_2O_8^{2-}$ in an acidic environment, the inclusion of Fe(II) salt as a catalyst proves to be highly effective. Both the cationic CTAB and anionic SDS retarded the Fe(II) catalyzed oxidation of Trp by $S_2O_8^{2-}$. TX-100, being a non-ionic surfactant has no significant effect on reaction rate.

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Conflict of interest

None of the authors has any potential or actual conflict of interest to disclose in relation to the published article.

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