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Hexacyanoferrate (III)- Mediated Oxidation of Organic Compounds in the Presence of Transition Metal Catalysts and Surfactants: A Review of Kinetic and Mechanistic Studies

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Abstract
This review provides a detailed kinetics investigation of the catalytic oxidation of organic compounds and selected amino acids in the presence of various transition metal catalysts and surfactants. The role of oxidizing agent and transition metal catalyst in influencing reaction rate and reaction pathways is critically examined. Special consideration is given to hexacyanoferrate (III) oxidant due to its selective one electron transfer capability and mechanistic versatility. In addition, the influence of surfactant on oxidation kinetics is systematically discussed, highlighting miceller catalysis, substrate -surfactant interaction, and changes in micro environmental properties such as polarity and electrostatic effect, overall, thus article consolidates existing kinetic and mechanistic insights to provide a clear understanding of metal-ion catalyzed and micelle mediated oxidation processes, while identify emerging trends and future research direction in the field.

Keywords: Kinetics, Hexacyanoferrate (III), Catalysis, Surfactants.

Introduction

Chemical kinetics provides essential insight into the rates and mechanisms of redox reactions, particularly those involving biologically relevant molecules such as amino acids. Organic compounds are a large class of chemical substances that contain carbon atoms bonded primarily with hydrogen, oxygen, nitrogen, sulfur, or halogens. Oxidation of organic compounds using hexacyanoferrate is an important method in synthetic chemistry, particularly when combined with transition metal catalysts. The most commonly used reagent is potassium ferricyanide, which acts as a mild and selective oxidizing agent. It undergoes a reversible redox transformation to potassium ferrocyanide after accepting electrons.

Amino acids are fundamental organic molecules that serve as the building blocks of proteins and play central roles in metabolism, cellular signaling and biochemical regulation. Each amino acid contains an amino group, a carboxyl group, and a distinctive side chain that determines its chemical behaviour and biological function[1-3]. Their diverse structures influence properties such as acidity, basicity, polarity, and reactivity, making amino acids essential subjects in chemical, biochemical, and pharmaceutical

research[4]. Understanding their structural features and reaction patterns provides insight into protein stability, enzyme function, and metabolic pathways, while also supporting applications in synthesis, biotechnology, and biomedical science[5-7].

The oxidation of amino acids has long been an important area of study in understanding biochemical redox reactions, metabolic pathways, and catalytic transformations [8].Using well-defined oxidants allows precise kinetic analysis and identification of rate-determining steps . Among the various oxidizing agents used in kinetic investigations, hexacynoferrate (III) stands out due to its stable structure, well-defined redox properties, and the ability to participate in outer-sphere electron-transfer reactions. Its predictable redox behaviour makes it a suitable model oxidant for probing the fundamental principles governing organic oxidation processes, particularly those involving biomolecules such as amino acids 9-12

In many systems, the presence of transition metal ions significantly modifies the oxidation behaviour of amino acids. Metals such as copper (II), iron (III), cobalt (II), and manganese (II) can act as catalytic centers by forming coordination complexes with amino acids and altering their electronic environments13-19. These metal substrate interactions often facilitate electron transfer either by lowering activation barriers or by stabilizing reaction intermediates. In the hexacyanoferrate (III) oxidative system, transition metals may introduce additional mechanistic routes, including inner-sphere electron transfer, ligand-assisted oxidation, or formation of transient metal amino acid chelates that enhance reactivity 20-25.The catalytic efficiency of these metals is largely governed by their redox potentials, ligand-exchange kinetics, and coordination preferences 26-28.

Studying the oxidation of amino acids by hexacyanoferrate(III) in the presence of various transition metals therefore provides valuable insight into the interplay between substrate structure, metal coordination, and redox activity 29-30. Such investigations not only deepen our understanding of reaction mechanisms relevant to biological oxidation processes but also contribute to the development of efficient catalytic systems for industrial and environmental applications. This research area continues to offer a versatile platform for exploring fundamental principles of chemical kinetics, coordination chemistry, and oxidation catalysis.

Surfactants introduce an additional layer of complexity and control in such systems. By forming micelles or other organized assemblies, surfactants modify the microenvironment around reactants, leading to changes in local concentration, polarity, and accessibility of catalytic sites 31-32. Anionic, cationic, and nonionic surfactants can differentially influence the binding of amino acids and metal ions, potentially accelerating or inhibiting the oxidation process 33-35. In micellar media, hexacyanoferrate(III) and metal–amino acid complexes may partition into distinct regions, altering the kinetics and providing insight into reactions in heterogeneous environments.

Studying the combined effects of transition metals and surfactants on the hexacyanoferrate(III) oxidation of amino acids offers deeper understanding of catalytic efficiency, microenvironmental control, and mechanistic diversity 36-42. These findings are valuable for biochemical modeling, environmental oxidation studies, and the design of advanced catalytic systems.

Oxidation of organic compound with hexacynoferrate (III) HCF(III) in presence of transition metal.

The oxidation of cyclic alcohols such as cyclopentanol and cyclohexanol by hexacyanoferrate(III) in aqueous alkaline medium in the presence of $RhCl_3$ has been reported by Praveen K. Tandon and co-worker 43. The results indicate that the reaction does not occur to a measurable extent under

uncatalyzed conditions, even after 98 h. However, the addition of trace amounts of $RhCl_3$ as a homogeneous catalyst significantly accelerates the reaction, leading to the formation of the corresponding dicarboxylic acids. It was observed that the rate of reaction increase proportionately with increasing concentrations of cyclopentanol and cyclohexanol. Stoichiometry of the reaction showed that eight moles of oxidant were required for the complete oxidation of one mole of organic substrate.

The oxidation of aromatic aldehydes by hexacyanoferrate (III) in presence of Ru(VI) as a catalyst in an alkaline medium has been investigated by C.I. Alcolado and Cowerkers 44. The reaction shows a complex order with respect to both the oxidant and the aromatic aldehyde, while it follows first-order kinetics with respect to Ru(VI). The proposed mechanism involves two catalytic cycles corresponding to the two active catalytic species. In each cycle, the Ru(VI) species interacts with the anion of hydrated benzaldehyde to form an intermediate complex, which subsequently decomposes to produce benzoic acid. Hexacyanoferrate (III) functions as a co-oxidant by regenerating the active Ru(VI) catalyst species, thereby maintaining the continuity of the catalytic cycle.

Gajala Tazwar et. Al reported the oxidation of ciprofloxacin (CIP) by hexacyanoferrate (III) (HCF) in presence of Cu(II) catalyst by spectrophotometrically in an aqueous alkaline medium at 40°C. The stoichiometric analysis reveals that the oxidation of one mole of CIP consumes two moles of HCF 45. Kinetic studies showed that the reaction follows first-order dependence on the concentration of HCF, whereas fractional order kinetics was observed with respect to the concentrations of CIP and OH^-.

A kinetic study of palladium (II)-catalyzed oxidation of pyrimidine derivative by hexacynoferrate (III) in aqueous alkaline medium has been studied by Ahmed Fawzy and Cowerkers 46 The reaction was found not to proceed in the absence of palladium (II), confirming the catalytic role of Pd (II) in the oxidation process. The reaction showed a first order kinetics in both [HCF] and Pd (II), and less than unit orders with respect to both [Pym-F] and [OH^-]. Increasing ionic strength and dielectric constant of the medium increased the reaction rate. The final oxidation products were identified as 2-aminopyrimidine, dimethylamine and carbon dioxide.

Oxidation of amino acids by hexacynoferrate (III) in the presence of transition-metal catalysts

Ahmed Fawzy reported a kinetic and mechanistic study of oxidation of L- tryptophan by potassium hexacyanoferrate (III) in presence of palladium (II) in aqueous perchloric acid medium 47. Kinetic studies revealed a first-order dependence on hexacyanoferrate (III), whereas fractional first-order dependences were observed for both L-tryptophan and palladium (II). The reaction showed a fractional second-order dependence on the hydrogen ion concentration ([H^+]). The final oxidation products were identified as indole-3-acetaldehyde, ammonium ion and carbon dioxide. Thus, a single protonated ferricyanide, H[Fe(CN)6] 2−, may be the reactive species in the present investigation. The reactive species of hexacyanoferrate (III) was identified as $H[Fe(CN)_6]^{2-}$, while the reactive species of palladium (II) was found to be $[PdCl_4]^{2-}$.

Kinetics and mechanism of Os(VIII)-catalyzed hexacyanoferrate (III) oxidation of α amino acids in alkaline medium has been studied by R. C. Acharya and coworkers 48 .The results indicated that the Os(VIII) catalyzed oxidation of amino acids by hexacyanoferrate (III) involves multisteps and proceeds through the intermediate formation of keto acids. Under the experimental alkaline conditions, $[OsO_4(OH)(H_2O)]^-$ is considered to be the effective catalytic species involved in the oxidation process.

S. K. Upadhay has been investigated the Kinetics and mechanism of osmium (VIII)-catalyzed oxidation of D-proline and L(–)-methionine by hexacyanoferrate (III) in alkaline medium 49. The results

indicated that the order in proline or methionine and OH^- decreases from unity to zero at higher concentrations of proline or methionine and OH^-, respectively. The stoichiometry of the reactions shown that each molecule of proline or methionine consumes two molecules of hexacyanoferrate(III) (two-electron transfer) in the presence of alkali and osmium(VIII).

Goel, A., and Sharma, S have been the oxidation of l-phenylalanine by hexacyanoferrate (III) catalyzed by Ir(III) by spectrophotometrically at 35 °C and at a constant ionic strength of 0.50 mol dm^{-3}. The major oxidation product was identified as phenylpyruvic acid using physico-chemical and spectroscopic methods 50. The reaction stoichiometry was found to be 2:1, indicating that two moles of hexacyanoferrate (III) react with one mole of phenylalanine. The reaction follows first-order kinetics with respect to hexacyanoferrate (III) and alkali concentration, while the order with respect to phenylalanine changes from first to zero with increasing substrate concentration.

In another study Savita Garg and Sakunj has been reported a kinetic and mechanistic study of Ir (III) catalyzed oxidation of methionine by HCF(III) in aqueous alkaline medium 51. The reaction follows first-order kinetics with respect to hexacyanoferrate (III), hydroxide ion, and iridium (III) concentrations. The reaction is also first order with respect to the substrate at lower concentrations, but the order approaches zero at higher substrate concentrations. An increase in ionic strength of the reaction medium results in a positive salt effect on the reaction rate.

Asghar, B. H and Co-workers have been investigated the oxidation of L-tryptophan by hexacyanoferrate (III) in alkaline medium in presence of copper (II) catalyst 52. The reaction was monitored by spectrophotometrically at a constant ionic strength of 0.5 mol dm^{-3} and at 25°C. The stoichiometry for both the reaction was 1:2 (Trp:HCF). The reactions exhibited first order kinetics with respect to [HCF] and less than unit orders with respect to [Trp] and $[OH^-]$. The catalyzed reaction exhibited fractional-first order kinetics with respect to $[Cu^{II}]$. The reaction rates were found to increase as the ionic strength and dielectric constant of the reaction medium increase.

Yadav, A et al. have been investigated an experimental and theoretical approach of electron transfer oxidation kinetics of copper (II) catalyzed reaction between lysine and HCF (III) 53. The oxidation of lysine by hexacyanoferrate (III) in alkaline medium proceeds at a very slow rate in the absence of Cu (II), whereas in the presence of Cu (II) markedly accelerates the reaction. The system exhibits a 2:1 stoichiometry, involving the consumption of two moles of hexacyanoferrate (III) per mole of lysine. Kinetic analysis reveals first-order dependence on hexacyanoferrate (III), lysine, hydroxide ions, and Cu (II). Additionally, the reaction rate is inhibited by the reduced product, hexacyanoferrate (II), indicating product inhibition and suggesting the involvement of intermediate complex formation in the reaction mechanism.

K. Sharanabasamma and Coworkers has been reported the kinetics and mechanism of ruthenium (III) catalyzed oxidation of L-proline by hexacyanoferrate(iii) in aqueous alkalin medium 54. The progress of reaction was monitored by spectrophotometrically at 30^0 C. The ruthenium (III)-catalyzed oxidation of L-proline by hexacyanoferrate (III) in aqueous alkaline medium was found to be first order with respect to both the oxidant and the catalyst, whereas it shows zero-order dependence on the substrate. The fractional order with respect to hydroxide ion concentration indicates the formation of a hydroxylated ruthenium (III) species, $[Ru(H_2O)_5(OH)]^{2+}$, in a pre-equilibrium step prior to the rate-determining step. The main oxidative product of L- proline was identified as L-glutamic acid.

The kinetics of oxidation of L-asparagine (Asn) by hexacyanoferrate (III) (HCF) has been investigated in alkaline medium in the absence and presence of silver(I) catalyst at a constant ionic strength of 0.5

mol dm^{-3} and at 20°C.by Ahmed Fawzy and Co-workers 55. The kinetics of both uncatalyzed and silver(I)-catalyzed oxidations were monitored spectrophotometrically. Both reactions exhibited first-order dependence on hexacyanoferrate (III), while the orders with respect to asparagine and hydroxide ion were less than unity. The silver(I)-catalyzed reaction also showed a first-order dependence on Ag(I). An increase in ionic strength and dielectric constant enhanced the rate of the uncatalyzed reaction, whereas it had no significant effect on the catalyzed reaction. The addition of the reaction product, hexacyanoferrate (II), did not influence the reaction rate. The catalyzed reaction is proposed to proceed through the formation of a silver(I)–asparagine intermediate complex, which reacts with the oxidant through an inner-sphere mechanism, followed by decomposition of the complex in the rate-determining step to yield the oxidation products α-formyl acetamide, ammonia, and carbon dioxide.

Heli, H. et al. reported a kinectics and mechanistic study of electrocatalytic oxidation of N-acetyl-l-cysteine (NAC) was studied on nanoparticles of iron(III) oxide core–cobalt hexacyanoferrate shell (Fe_2O_3@CoHCF)-modified carbon paste electrode (cs-MCPE) 56. Voltammetric studies indicated that NAC was oxidized via a surface mediation electrocatalytic mechanism by Fe_2O_3@CoHCF. The catalytic rate constant, the electron-transfer coefficient and the diffusion coefficient involved in the electrooxidation process of NAC on Fe_2O_3@CoHCF were reported. Based on the electrocatalytic efficiency of Fe_2O_3@CoHCF, cs-MCPE was employed for the ultrasensitive sensing of the trace amounts of NAC. The proposed amperometry method was also applied to the analysis of commercial tablets and injection samples

Kinetics and mechanism of osmium (VIII) catalysed oxidation of formic acid by hexacyanoferrate (III) in aqueous alkaline medium has been reported by Sharma G and Cowrkers 57. The kinetics of the reaction were monitored by estimating hexacyanoferrate (III) at 420 nm employing spectronic 21 without any interference from osmium (VIII) and its reduction product. The species $[OS\ O_4\ (OH)_2\ ]^{2-}$ has been considered to be the reactive form of the catalyst.

Catalytic oxidation of organic compound by hexacyanoferrate (III) in the presence of surfactant

Baraka, R. M. and coworkers have been reported The oxidation of phenyl hydrazinium chloride ($PhNHNH_2$) by hexacyanoferrate(III) ($[Fe(CN)_6]^{3-}$) in aqueous solutions 58. The oxidation of phenyl hydrazine ($PhNHNH_2$) by hexacyanoferrate (III) [Fe(CN)6]3−[Fe(CN)₆]^{3−}[Fe(CN)6]3− has been systematically investigated in aqueous medium, both in the absence and presence of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) micelles. The reaction exhibits saturation kinetics with respect to phenyl hydrazine, attaining a limiting rate at substrate concentrations ≥ 0.005 M, indicating the formation of a reactive intermediate complex prior to the rate-determining electron transfer step. Kinetic analysis enabled the evaluation of the ion-pair (or intermediate complex) formation constant (K_{IP}) and the electron transfer rate constant (k_{et}).

The effect of cationic surfactant cetyltrimethylammonium bromide (CTAB) and anionic surfactant sodium dodecyl sulphate (SDS) on the rate of oxidation of D-penicillamine by alkaline hexacyanoferrate (III) has been studied by Khan, A. A. P and Coworkes 59.The effect of CTAB and SDS on the rate of reaction has been observed at even below the critical micelle concentration (CMC) of the surfactants, indicating binding of the substrate with the surfactants. Activation parameters have also been evaluated in the absence and presence of surfactant.

Khan, A. A. P et al investigated the effect of sodium dodecyl sulfate (SDS) on the oxidation of levothyroxine (LVT) by hexacyanoferrate (III) in alkaline medium using spectrophotometric techniques

at varying temperatures 60. The reaction exhibits complex kinetic behavior with first-order dependence on both LVT and hydroxide ion concentration. A notable alteration in the reaction rate is observed around the critical micelle concentration (CMC) of SDS, indicating significant substrate–micelle interactions. The binding parameters, evaluated using the Menger–Portnoy model, suggest that micellar environments play a crucial role in modulating the reaction pathway and enhancing the reaction rate.
Ratna shukla et al. studied the oxidation of ascorbic acid by hexacynoferrate (III) in presence of cationic surfactant viz. cetyltrimethylammonium bromide (CTAB) 61. An inhibition effect of CTAB (below its critical micelle concentration) on the rate of oxidation has been observed. The spectrophotometric and kinetic data indicated a 1:1 premicellar association between substrate and surfactant.

Catalytic oxidation of amino acid with hexacyanoferrate in the presence of surfactant-
Srivastava, A and coworkers have been investigated Ru(III) promoted oxidation of L-phenylalanine (L-PheAla) by $[Fe(CN)_6]^{3-}$ in anionic sodium dodecyl sulfate (SDS) micellar medium by recording the decrease in absorbance at 420 nm corresponding to $[Fe(CN)_6]^{3-}$ using an UV–visible spectrophotometer 62. Under pseudo-first-order condition, the course of the reaction was studied as a function of $[Fe(CN)_6^{3-}]$, ionic strength, $[OH^-]$, [SDS], $[Ru^{3+}]$, [L-PheAla] and temperature by changing one variable at a time. The results indicated that $[OH^-]$, [SDS], and [L-PheAla] are the crucial parameters that have an appreciable influence on the reaction rate. The reaction exhibits first-order kinetics in concentration ranges of Ru(III), $[Fe(CN)_6]^{3-}$ and at low [L-PheAla] and $[OH^-]$ concentrations. It was observed that the reaction rate was almost 10 times faster in SDS micellar medium than in aqueous medium.
The Ru (III)-catalyzed oxidation of L-glutamic acid (Glu) by hexacyanoferrate (III) has been kinetically investigated in cetyltrimethylammonium bromide (CTAB) micellar medium by Srivastava and Coworkers 63. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance at 420 nm, corresponding to hexacyanoferrate (III). Under the examined concentration ranges of Ru (III) and oxidant, and at lower concentrations of Glu and hydroxide ions, the system exhibits first-order kinetic behavior. The observations highlight the catalytic role of Ru (III) and the influence of the micellar environment on the reaction kinetics.
Srivastava et al Moscow: Pleiades Publishing reported the kinetics of L-leucine (Leu) oxidation by hexacyanoferrate (III) in a cetyltrimethylammonium bromide (CTAB) micellar medium 64. The study demonstrated a 2:1 stoichiometric interaction between hexacyanoferrate (III) and Leu, with a first-order dependence on the oxidant concentration. The reaction exhibits fractional first-order kinetics with respect to Leu, hydroxide ions, and Cu (II) over the investigated concentration ranges. Furthermore, the presence of CTAB significantly enhances the reaction rate, emphasizing the catalytic role of the micellar environment in influencing the reaction mechanism.
The kinetics of Cu(II) catalysed oxidation of L-valine by hexacyanoferrate(III) in CTAB micellar medium were investigated by measuring the decline in absorbance at 420 nm by Srivastava, A., and coworkers Srivastava, 65 .The results reveal that the concentration of cetyltrimethylammonium bromide (CTAB) plays a critical role in governing the reaction rate. A 2:1 stoichiometric interaction between hexacyanoferrate (III) and valine (Val) has been established, with the reaction showing first-order dependence on the oxidant concentration. However, within the investigated ranges of Cu (II), hydroxide ions, and valine, the system exhibits fractional first-order kinetics.
Srivastava et al. Srivastava reported the kinetics of Os(VIII)-catalyzed oxidation of L-tryptophan (Trp) by hexacyanoferrate (III) in CTAB micellar medium, monitored spectrophotometrically at 420 nm 66.

The study revealed that CTAB, Trp, and hydroxide ion concentrations significantly influence the reaction rate, whereas the rate remains independent of hexacyanoferrate (III), which primarily functions in the regeneration of Os(VIII). Under the investigated conditions, the reaction exhibits first-order dependence on Os(VIII), Trp, and hydroxide ions at lower concentrations, but deviates to fractional order at higher substrate and alkali concentrations, indicating the involvement of complex mechanistic pathways.

Conclusion

The kinetic study of the oxidation of various organic compounds including amino acids by hexacynoferrate (III), [Fe(CN)6]3-, provides valuable insight into the role of reaction medium, transition-metal catalysts, and surfactants in governing reaction pathways and rates. In the absence of any catalyst or additive, the oxidation of organic compounds by hexacynoferrate is generally slow, particularly in aqueous medium. The reaction typically follows first-order kinetics with respect to hexacynoferrate and fractional or first-order dependence on the amino acid concentration. The slowness of the uncatalyzed reaction indicates a high activation energy and an outer-sphere electron-transfer mechanism, in which direct interaction between the oxidant and the amino acid is limited.

The introduction of transition-metal catalysts such as Cu(II), Ru(III), Os(VIII), silver(I) etc. markedly enhances the rate of oxidation. The review shows an increase in the observed rate constant with increasing metal-ion concentration, confirming the catalytic role of these ions. The catalytic action is attributed to the formation of transient metal–amino acid complexes, which facilitate inner-sphere electron transfer. The catalyzed reactions usually exhibit lower activation energies and higher reaction rates compared to the uncatalyzed system, while maintaining first-order dependence on the oxidant.

Surfactants introduce an additional level of control by modifying the reaction environment rather than participating directly in redox chemistry. Above their critical micelle concentration, surfactants such as CTAB, SDS form micelles that create micro heterogeneous media. Kinetic studies reveal that cationic surfactants generally enhance the oxidation rate by electro statically attracting anionic species such as hexacynoferrate and deprotonated amino acids to the micellar interface. In contrast, anionic surfactants often retard the reaction due to electrostatic repulsion, while nonionic surfactants show moderate effects governed mainly by solubilization and polarity changes. The observed rate behavior in surfactant media is well explained by the micellar pseudo phase model, which considers parallel reactions in aqueous and micellar phases. When transition-metal catalysts and surfactants are present simultaneously, synergistic effects are often observed. The miceller environment can stabilize metal–substrate complexes and reactive intermediates, further enhancing the efficiency of electron transfer. Overall, the kinetic study demonstrates that the oxidation of amino acids by hexacyanoferrate (III) is highly sensitive to the reaction medium. Transition-metal catalysts lower the activation barrier through inner-sphere mechanisms, while surfactants fine-tune reactant distribution and micro environmental properties. These findings not only deepen the understanding of redox kinetics in solution but also provide useful models for mimicking enzyme-like behavior in biochemical and industrial oxidation processes.

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