

Ru(III) Catalyzed Oxidation of Ciprofloxacin by Iron(III): A Kinetic and Mechanistic Approach

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Oxidation of fluoroquinolone class antibiotic *i.e.*, ciprofloxacin using hexacyanoferrate(III) in the presence of ruthenium catalyst has been investigated spectrophotometrically in an aqueous alkaline medium at room temperature. The main reaction product was identified by LC-MS was 4-cyclopropyl-7-fluoro-2-hydroxy-6-(piperazin-1-yl)naphthalen-1(4*H*)-one. Stoichiometric ratio obtained was 1:2, that is for each mole of ciprofloxacin two moles of hexacyanoferrate(III) are required for their complete oxidation. The reaction exhibited unit order with respect to hexacyanoferrate(III) and Ru (catalyst) and it was found to be less than unit order for [OH⁻] and ciprofloxacin. Considering the possible reactive species of reactant and a most probable kinetic mechanism have been envisaged. Mechanism was proposed for the reaction using the activation parameters and thermodynamic quantities calculated with respect to the slow step mechanism.

Keywords: Ciprofloxacin, Kinetics, Hexacyanoferrate(III), Ruthenium.

INTRODUCTION

Existence of pharmaceuticals like antibiotics in the aquatic environment lead to long-term life threatening risks such as toxicity to aquatic animals and the disturbance of endocrine systems of higher organisms [1,2]. Antibiotics are of great demand as both human and veterinary medicines and their over-use increased their presence in water which is of concern due to the development of antibiotic resistant bacteria [3].

Ciprofloxacin (CIP), chemically is {1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazine-1-yl)-quinolone-3-carboxylic acid} (Fig.1). A number of bacterial infections including joint and bone infections, abdominal infections, respiratory tract infections, skin infections and urinary tract infections, to name few are being treated using this antibiotic. It is also preferred to treat people who have been exposed to anthrax or certain types of plague. It is a second generation fluoroquinolone antimicrobial agent with a large spectrum of activity against many Gram-positive and Gram-negative aerobic and anaerobic bacteria. Also, a member of fluoroquinolone group is used world wide as a human and veterinary medicine [4].

A large number of antibacterial drugs are discharged in water bodies which directly reach into aquatic environment and

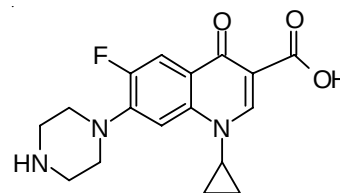


Fig. 1. Structure of ciprofloxacin

indirectly into animals and human being [5]. Wastewater analysis have detected the presence of fluoroquinolones in various range from dm^{-3} to ng dm^{-3} [6]. Due to their harmful effect on human health, these antibacterial compounds have been classified under the class of pollutants [7]. The oxidative transformation of fluoroquinolones antibacterial agents in a water treatment process plays an important role in this concern.

A powerful catalyst, ruthenium(III) is known to be in function in various redox reactions particularly in alkaline medium [8-11]. A complicated reaction mechanism for catalysis has been figured out. This is due to the formation of different intermediate complexes, free radicals and different oxidation states of ruthenium. An outer sphere mechanism is observed for kinetics of fast reactions between ruthenate(VII), RuO_4^- , and manganate(VI) [12]. The rapid exchange between MnO_4^{2-} and

MnO₄⁻ has been studied by a variety of techniques [13]. The catalyzed reaction between ciprofloxacin and hexacyanoferrate(III) in alkaline medium using copper as catalyst has been previously studied [14]. A microamount of ruthenium(III) is enough to catalyze the reaction in alkaline medium. Thus, Ru(III) catalyzed oxidation of ciprofloxacin by hexacyanoferrate(III) in aqueous alkaline medium mechanism finds to be more interesting thus we have selected the present study.

Hexacyanoferrate(III) oxidizes both inorganic and organic compounds in acidic, basic and neutral medium [15,16]. It has a redox potential of +0.45V for [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ couple in alkaline medium leading to final product hexacyanoferrate (II), a stable product [17-19]. It acts as a hydrogen atom abstractor [20] and free radical generator [21]. There is a central iron ion at center which is surrounded by six negative CN⁻ ions in an octahedral arrangement.

A literature survey revealed that ciprofloxacin oxidation was carried out using oxidants like KMnO₄ both in acidic and alkaline medium, ozone free chlorine, ClO₂ and HCF in presence of copper catalyst [14,22-26]. However, oxidation of ciprofloxacin using hexacyanoferrate(III) using micro amounts of ruthenium catalyst showed a doubled increase in rate and hence the titled reaction is accepted to understand the mechanism of reaction and active species involved in ruthenium catalyzed oxidation of ciprofloxacin.

EXPERIMENTAL

All the chemicals used in the oxidation study were of analytical grade. All the reaction solutions were prepared using double distilled water. Solution of ciprofloxacin (m.w.: 331.346 g/mol) was always prepared freshly just before the experiment. To facilitate the dissolution of ciprofloxacin, a few drops of 1 M KOH were added to the stock solution [27].

The stock solution of oxidizing agent hexacyanoferrate(III) (Merck) was prepared by dissolving K₃[Fe(CN)₆] in double distilled water and this solution was standardized iodometrically [28]. Accurate amount of RuCl₃ (S.D. Fine-Chem.) was weighed out, dissolved in 0.20 mol dm⁻³ HCl and made up to the mark and this ruthenium(III) solution was ascertained by EDTA titration [29].

Sodium hydroxide (Merck) were used to provide the required basicity and NaNO₃ were used to maintain the ionic strength. Sodium hydroxide is standardized with potassium hydrogen phthalate using phenolphthalein as indicator. Each and every time fresh solutions were used for kinetic run. Corning glass were used for storing the utilized reagents and for studying the kinetics of reaction unless otherwise specified. A double beam UV-visible spectrophotometer fitted with thermostatic compartment and a recorder was used for recording the disappearance of colour during the kinetic study.

Kinetic measurements: Kinetic studies were experimented under pseudo-first order conditions, where the drug concentration is excess over [HCF], at a constant ionic strength in alkaline medium at room temperature. The oxidant was pipetted out into the drug, which also contained the required quantities of NaNO₃, NaOH and ruthenium. The reaction progress was understood by measuring the variation in colour using spectrophotometrically at 420 nm range where no other major absorption take

place. The decrease in the concentration of HCF(III) with the decrease in intensity of colour was indicated by UV spectra (Fig. 2). The application of Beer's law of HCF at 420 nm has been verified giving = 1050 dm³/mol/cm [30].

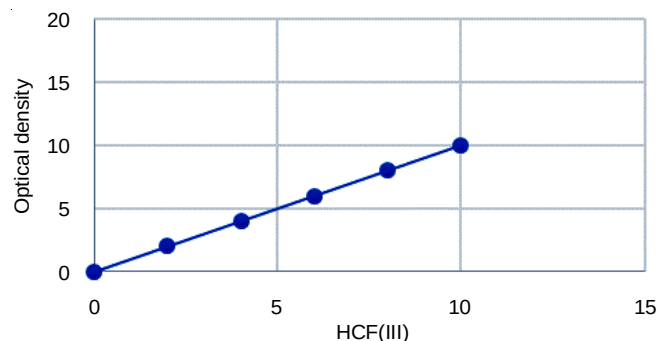
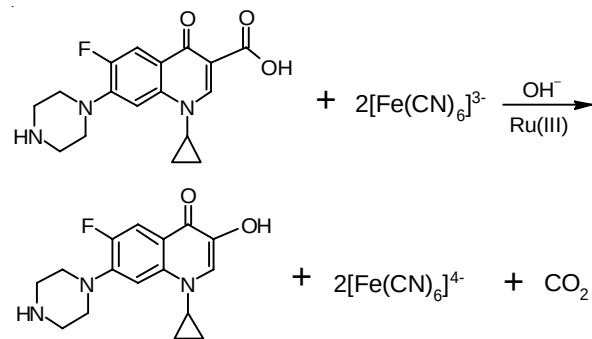


Fig. 2. Verification of Beer's law for hexacyanoferrate(III) at 420 nm in 0.1 mol/dm³ NaOH

The *k*_{obs} (pseudo- first order rate constant) was calculated from the slope of logarithm of absorbance *versus* time. The pseudo-first order plot was linear upto 80 % completion of oxidation study.

RESULTS AND DISCUSSION

Stoichiometry: The stoichiometric analysis was done by keeping the reaction mixtures mainly the drug and oxidant in various ratios for 24 h at room temperature in a closed vessel while keeping all other reactant concentration constant (0.1 N NaOH, 0.05 N NaNO₃, 5 × 10⁻⁶ mol/dm³ ruthenium). The results indicated that 1 mol of ciprofloxacin reacts with 2 mol of HCF and following reaction is generated as:



For product analysis, acid was added to the reaction mixture and extracted with ethyl acetate. The oxidized product 4-cyclopropyl-7-fluoro-2-hydroxy-6-(piperazin-1-yl)naphthalen-1(4H)-one was identified with the help of TLC and LC-MS (Fig. 3) analysis.

From LC-MS, a molecular ion of *m/z* 303 amu was identified which correspond to the product. The peak for ciprofloxacin is at 332 and 303 corresponds to the decarboxylation of quinolones ring to yield 4-cyclopropyl-7-fluoro-2-hydroxy-6-(piperazin-1-yl)naphthalen-1(4H)-one product.

Dependence of hexacyanoferrate(III): The effect of varying concentration of oxidant was studied. Hexacyanoferrate(III) concentration varied from 0.5 × 10⁻⁴ to 4.5 × 10⁻⁴ mol/dm³ in the reaction mixture keeping all other reactant concentration

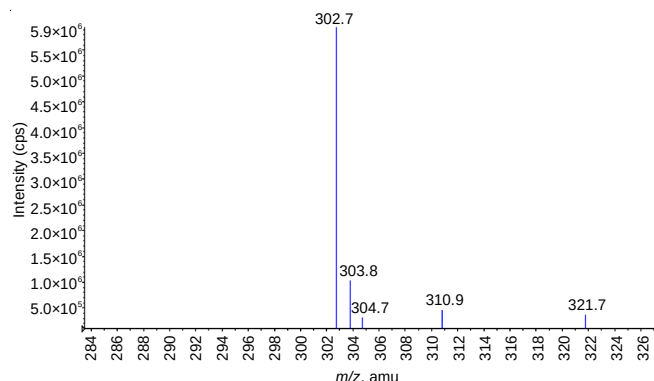


Fig. 3. LC-MS spectra of the oxidation product of CIP vs. HCF(III)

and conditions constant *i.e.* ciprofloxacin 2.5×10^{-3} mol/dm³, NaOH 0.1N, NaNO₃ at 0.05 N and ruthenium at 5×10^{-6} mol/dm³. Log absorbance *versus* time plot was found to be linear (figure not shown) indicating the reaction is first order with respect to concentration of hexacyanoferrate(III).

Dependence of ciprofloxacin: The dependence of ciprofloxacin on the oxidation reaction was understood by changing the concentration of ciprofloxacin in ruthenium catalyzed study from 0.5×10^{-4} to 4.5×10^{-4} mol/dm³ at constant concentration of HCF(III) 2.5×10^{-4} mol/dm³, NaOH 0.1 N, NaNO₃ at 0.05 N, Ru(III) 5×10^{-6} mol/dm³ at 25 °C. A steady increase in rate was observed (Table-1). A plot of $\log k_{\text{obs}}$ *versus* $\log [\text{CIP}]$ was linear and the slope was found to be 0.35, thus indicating fractional order dependence.

Dependence of medium: The hydroxyl ion concentration effect on the present oxidation study on the rate was conducted by varying the concentration of NaOH from 0.01 to 0.25 N at fixed concentration of other reactant ciprofloxacin 2.5×10^{-3} mol/dm³, HCF(III) 2.5×10^{-4} mol/dm³, NaNO₃ at 0.05 N, Ru(III) 5×10^{-6} mol/dm³ at 25 °C. Table-1 shows an increase in k_{obs} value with concentration of OH⁻. A plot of $\log k_{\text{obs}}$ *versus* $\log [\text{OH}^-]$ gave a fractional slope 0.63.

Dependence of catalyst Ru(III): The [Ru(III)] varied from 1.5×10^{-6} to 25×10^{-6} mol/dm³ at constant concentration of ciprofloxacin 2.5×10^{-3} mol/dm³, HCF(III) 2.5×10^{-4} mol/dm³, NaOH 0.1 N, NaNO₃ at 0.05 N at constant temperature. The rate of reaction show an abrupt rise with increase in Ru(III) concentration (Table-1). A plot of rate constant k_{obs} against Ru(III) concentration gave unit order with respect to ruthenium.

Effect of ionic strength and dielectric constant: Sodium nitrate concentration varied from 0.025 to 0.1 mol/dm³ at 25 °C. It was observed of having no substantial effect on rate of reaction with change of NaNO₃ concentration.

Effect of added product: Ferrous sulphate was added to the reaction mixture from varying concentration keeping other reactants concentration constant and conditions same, but no change was observed in the kinetic reaction.

Presence for free radicals: Acrylonitrile was added to reaction mixture which contained an oxidant, HCF and reductant, ciprofloxacin along with alkali and ionic medium and was kept for 5 undisturbed. Then, it was diluted with methanol where

TABLE-1
FOR RATE CONSTANT OBSERVED AND CALCULATED FOR THE STUDY OF VARIATION OF
[CIP], [HCF], [NaOH], [NaNO₃] AND [Ru(III)] ON THE OXIDATION OF CIPROFLOXACIN AT 25 °C

[CIP] $\times 10^{-3}$ (mol dm ⁻³)	[HCF] $\times 10^{-4}$ (mol dm ⁻³)	OH ⁻ (mol dm ⁻³)	NaNO ₃ (mol dm ⁻³)	[Ru] $\times 10^{-6}$ (mol dm ⁻³)	$k_{\text{obs}} \times 10^{-3}$ (s ⁻¹)	$k_{\text{ca}} \times 10^{-3}$ (s ⁻¹)
[CIP]						
0.5	2.5	0.10	0.050	5.0	16.4	15.9
1.5	2.5	0.10	0.050	5.0	17.4	15.9
2.5	2.5	0.10	0.050	5.0	29.5	15.9
3.5	2.5	0.10	0.050	5.0	31.7	15.9
4.5	2.5	0.10	0.050	5.0	34.9	15.9
[HCF]						
2.5	0.5	0.10	0.050	5.0	55.2	55.7
2.5	1.5	0.10	0.050	5.0	27.9	28.0
2.5	2.5	0.10	0.050	5.0	29.5	29.8
2.5	3.5	0.10	0.050	5.0	31.0	31.5
2.5	4.5	0.10	0.050	5.0	33.0	33.2
[NaOH]						
2.5	2.5	0.01	0.050	5.0	12.0	11.5
2.5	2.5	0.05	0.050	5.0	15.0	15.2
2.5	2.5	0.10	0.050	5.0	29.5	29.8
2.5	2.5	0.15	0.050	5.0	41.8	40.2
2.5	2.5	0.25	0.050	5.0	40.3	44.1
[NaNO ₃]						
2.5	2.5	0.10	0.025	5.0	20.1	20.5
2.5	2.5	0.10	0.050	5.0	29.5	28.2
2.5	2.5	0.10	0.100	5.0	24.6	24.6
[Ru(III)]						
2.5	2.5	0.10	0.050	1.5	5.2	5.0
2.5	2.5	0.10	0.050	2.5	10.3	11.3
2.5	2.5	0.10	0.050	5.0	29.5	30.5
2.5	2.5	0.10	0.050	10.0	32.6	31.7
2.5	2.5	0.10	0.050	25.0	41.8	42.5

a white precipitate was obtained, indicating the involvement of free radical in the reaction [31,32].

Effect of temperature: The temperature effect on ciprofloxacin oxidation with HCF using ruthenium as catalyst was studied at 308 to 323 K at fixed concentration of substrate, oxidant medium, ionic strength and catalyst (ciprofloxacin oxidation at 2.5×10^{-3} mol/dm³, HCF(III) 2.5×10^{-4} mol/dm³, NaOH at 0.1 N, NaNO₃ at 0.05 N and Ru(III) 5×10^{-6} mol/dm³). The energy of activation is obtained from the slope of the linear Arrhenius plot $\log k$ vs. $1/T$ and the value was found to be 24.9 kJ/mol. Other thermodynamics parameters were calculated using Eyrings equation and tabulated in Table-2 [33-35].

TABLE-2 VARIATION OF RATE CONSTANT WITH TEMPERATURE FOR CIP OXIDATION AT 2.5×10^{-3} mol/dm ³ , HCF(III) 2.5×10^{-4} mol/dm ³ , NaOH AT 0.1 N, NaNO ₃ AT 0.05 N AND Ru(III) 5×10^{-6} mol/dm ³	
Temperature (K)	k (dm ³ mol ⁻¹ s ⁻¹)
308	12.3
313	14.5
318	16.4
323	18.2
Activation parameters	Values
E _a (kJ mol ⁻¹)	24.9
ΔH [‡] (kJ mol ⁻¹)	21.5
ΔS [‡] (JK ⁻¹ mol ⁻¹)	-305.5
ΔG [‡] (kJ mol ⁻¹)	85.55

Oxidation of ciprofloxacin using hexacyanoferrate(III) is a slow reaction which gets accelerated in the presence of micro amounts of ruthenium catalyst. The stoichiometry between ciprofloxacin and HCF was found to be 1:2, in the presence of Ru(III) catalyst and the orders were unit order with respect to HCF(III) and catalyst also fractional order with respect to substrate and alkali concentration. Ru(III) in alkaline medium exists as hydroxylated species $[\text{Ru}(\text{OH}) \times (\text{H}_2\text{O})_{6-x}]_{(3-x)}$ where $x < 6$ [36-38]. The intermediate complex is formed by the interaction of anionic form of ciprofloxacin and Ru(III). This formed complex undergoes a slow reaction with HCF leading to the product. Hydroxyl ion concentration has a direct influence on reaction rate. Based on observation and experimental results mechanism is proposed for the scheme and rate law is derived. The non-zero intercept for plot between $[\text{Ru(III)}]/k_{\text{obs}}$ versus $1/[\text{CIP}]$, helps in the prediction of formation of complexes.

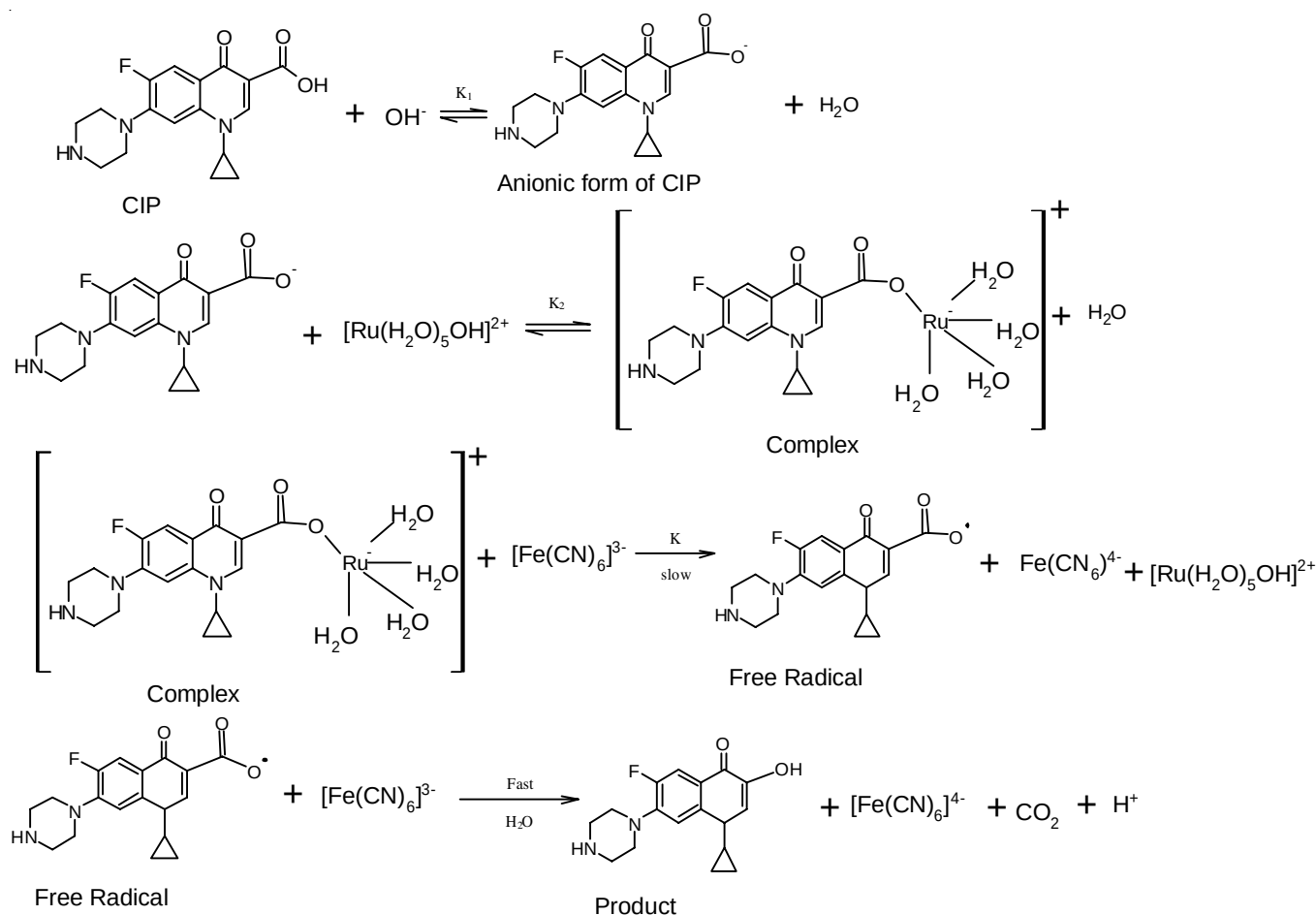
The following rate equation can be derived from **Scheme-I**.

The following rate equation is derived based on rate equation:

$$\text{Rate} = \frac{-d[\text{HCF}]}{dt} = k[\text{C}][\text{HFC}] \quad (2)$$

The equilibrium constant, K_1

$$K_1 = \frac{[\text{CIP}]}{[\text{CIP}^-]_F[\text{OH}^-]_F} \quad (3)$$



Scheme-I: Proposed mechanism for the Ru(III) catalysed oxidation of ciprofloxacin using hexacyanoferrate(III)

where, 'F' is the free concentration.

$$[\text{CIP}^-] = K_1[\text{CIP}]_F[\text{OH}^-]_F$$

The equilibrium constant K_2

$$K_2 = \frac{[\text{C}]}{[\text{CIP}^-][\text{Ru(III)}]_F}$$

$$[\text{C}] = K_2[\text{CIP}^-][\text{Ru(III)}]_F$$

Substituting for $[\text{CIP}^-]$

$$[\text{C}] = K_1 K_2 [\text{CIP}]_F [\text{OH}^-]_F [\text{Ru(III)}]_F \quad (4)$$

Substituting eqn. 4 into eqn. 2:

$$\text{Rate} = k K_1 K_2 [\text{CIP}]_F [\text{OH}^-]_F [\text{Ru(III)}]_F [\text{HCF}] \quad (5)$$

The total concentration 'T' of CIP is given by

$$[\text{CIP}]_T = [\text{CIP}]_F + [\text{CIP}^-] + [\text{C}] \quad (6)$$

Substituting eqn. 3 and eqn. 4 into eqn. 6:

$$[\text{CIP}]_T = [\text{CIP}]_F + K_1 [\text{CIP}]_F [\text{OH}^-]_F + K_1 K_2 [\text{CIP}]_F [\text{OH}^-]_F [\text{Ru(III)}]_F \quad (7)$$

$$[\text{CIP}]_T = [\text{CIP}]_F \{ 1 + K_1 [\text{OH}^-]_F + K_1 K_2 [\text{OH}^-]_F [\text{Ru(III)}]_F \} \quad (8)$$

From the eqn. 8:

$$[\text{CIP}]_F = \frac{[\text{CIP}]_T}{1 + K_1 [\text{OH}^-]_F + K_1 K_2 [\text{OH}^-]_F [\text{Ru(III)}]_F} \quad (9)$$

$K_1 K_2 [\text{OH}^-]_F [\text{Ru(III)}]_F$ term is neglected as the ruthenium concentration is in micro level. Therefore, eqn. 9 is simplified:

$$[\text{CIP}]_F = \frac{[\text{CIP}]_T}{1 + K_1 [\text{OH}^-]_F} \quad (10)$$

The total concentration of Ru(III) can be given as:

$$[\text{Ru(III)}]_T = [\text{Ru(III)}]_F + [\text{C}] \quad (11)$$

$$[\text{Ru(III)}]_T = [\text{Ru(III)}]_F \{ 1 + K_1 K_2 [\text{CIP}]_F [\text{OH}^-]_F \} \quad (12)$$

$$[\text{Ru(III)}]_F = \frac{[\text{Ru(III)}]_T}{1 + K_1 K_2 [\text{CIP}]_F [\text{OH}^-]_F} \quad (13)$$

Considering the concentration of OH^-

$$[\text{OH}^-]_F = [\text{OH}^-]_T \quad (14)$$

$$\text{Rate} = \frac{k K_1 K_2 [\text{CIP}]_T [\text{OH}^-]_T [\text{Ru(III)}]_T [\text{HCF}]}{(1 + K_1 [\text{OH}^-]_T)(1 + K_1 K_2 [\text{CIP}]_T [\text{OH}^-]_T)}$$

Omitting subscripts T and F

$$\text{Rate} = \frac{k K_1 K_2 [\text{CIP}] [\text{OH}^-] [\text{Ru(III)}] [\text{HCF}]}{(1 + K_1 [\text{OH}^-])(1 + K_1 K_2 [\text{CIP}] [\text{OH}^-])} \quad (15)$$

$$\text{Rate} = \frac{k K_1 K_2 [\text{CIP}] [\text{OH}^-] [\text{Ru(III)}] [\text{HCF}]}{1 + K_1 K_2 [\text{CIP}] [\text{OH}^-] + K_1 [\text{OH}^-] + K_1^2 K_2 [\text{OH}^-]^2 [\text{CIP}]} \quad (16)$$

$$\text{Rate} = \frac{k K_1 K_2 [\text{CIP}] [\text{OH}^-] [\text{Ru(III)}] [\text{HCF}]}{1 + K_1 K_2 [\text{CIP}] [\text{OH}^-] + K_1 [\text{OH}^-]} \quad (17)$$

The term $K_1^2 K_2 [\text{OH}^-]^2 [\text{CIP}]$ is neglected as the $[\text{CIP}]$ is very low.

From the eqn. 2:

$$\text{Rate} = \frac{-d[\text{HCF}]}{dt} = k_{\text{obs}} [\text{HCF}] \quad (18)$$

Comparing eqns. 17 and 18, we get:

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{HCF}]} = \frac{k K_1 K_2 [\text{CIP}] [\text{OH}^-] [\text{Ru(III)}] [\text{HCF}]}{1 + K_1 K_2 [\text{CIP}] [\text{OH}^-] + K_1 [\text{OH}^-]} \quad (19)$$

Eqn. 19 can be rearranged:

$$\frac{[\text{Ru(III)}]}{k_{\text{obs}}} = \left(\frac{1}{k K_1 K_2 [\text{OH}^-]} + \frac{1}{k K_2} \right) \frac{1}{[\text{CIP}]} + \frac{1}{k} \quad (20)$$

The above linear equation of the form $y = mx + c$, so when the graph is plotted between $[\text{Ru(III)}]/k_{\text{obs}}$ and $1/[\text{CIP}]$ gives a positive intercept. And the rate constant for the slow step is obtained from intercept (Table-2).

$$\frac{[\text{Ru(III)}]}{k_{\text{obs}}} = \left(\frac{1}{k K_1 K_2 [\text{CIP}]} \right) \frac{1}{[\text{OH}^-]} + \frac{1}{k K_2 [\text{CIP}]} + \frac{1}{k} \quad (21)$$

The values of equilibrium constant, K_1 and K_2 are evaluated from the intercepts and slope of the plots of $[\text{Ru(III)}]/k_{\text{obs}}$ and $1/[\text{CIP}]$ and $[\text{Ru(III)}]/k_{\text{obs}}$ and $1/[\text{OH}^-]$ and is found to be $15.3 \text{ dm}^3 \text{ mol}^{-1}$ and $9.2 \text{ dm}^3 \text{ mol}^{-1}$, respectively (figure not shown).

The entropy of activation ($\Delta S^\ddagger$) tends to be more negative for reaction involving inner-sphere mechanism, whereas the reactions of positive $\Delta S^\ddagger$ values proceed via an outer-sphere mechanism [39-41]. In the present study the high values of $\Delta S^\ddagger$ (Table-2) expresses the mechanism is one electron transfer of inner-sphere nature confirming there is decrease in the randomness during the reaction process. Hence the formed intermediate complex is found to be more ordered than the reactants due to loss of degrees of freedom.

Conclusion

The oxidation of ciprofloxacin using hexacyanoferrate(III) in the presence of micro quantities of ruthenium helps in degradation of the antibiotic present in environment. The reaction was found to be unit order with respect to HCF(III) and ruthenium also fractional order with respect to CIP and OH^- concentration. The reaction mechanism involve complex formation and free radical. Stoichiometry was found to be 1:2, that is 1 mol of CIP requires 2 mol of HCF. The major product was found to be 4-cyclopropyl-7-fluoro-2-hydroxy-6-(piperazin-1-yl)naphthalen-1(4H)-one which has detected by LC-MS. Activation parameters were evaluated with respect to slow step of reaction schemes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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