Bulgarian Chemical Communications, Volume 57, Issue 3 (pp. 206-212) 2025 DOI: 10.34049/bcc.57.3.PJ-RS

Unraveling the mechanism of ruthenium (III)-catalyzed aspirin oxidation by hexacyanoferrate(III): kinetic and spectrophotometric approach

B. Gupta[1], Nikita[2], A. Rolaniya[2], A. Yadav[2], P. Jain[3], R. Sailani[2]*

[1]*Public health Lab Analyst, Technical Manager for NABL Accreditation, Food Safety and Standards Laboratory, Alwar, Rajasthan, India*
[2]*Chemical Kinetics Laboratory, Department of Chemistry, University of Rajasthan, Jaipur, Rajasthan, Indıa-302004*
[3]*Department of Chemistry, IIS-Deemed to be University, Jaipur, Rajasthan, India-302004*

Accepted: August 17, 2024

The redox reaction between aspirin and hexacyanoferrate (III), catalyzed by ruthenium (III) in alkaline medium, was thoroughly investigated. The reaction kinetics exhibit a complex dependence on both hydroxide ion and aspirin concentrations, while the reaction order with respect to the oxidant and catalyst is found to be unity. Based on the kinetic results, a plausible reaction mechanism was proposed, and the derived rate law successfully accounts for all experimental observations. Kinetic parameters were evaluated under varying conditions, and activation as well as thermodynamic parameters were accurately determined using the Arrhenius and Eyring equations.

Keywords: Aspirin; hexacyanoferrate (III); ruthenium (III); oxidation kinetics, reaction mechanism.

INTRODUCTION

Aspirin is acetyl salicylic acid and is an important drug with wide applications. It is a nonsteroidal analgesic,antiinflammatory and antipyretic agent which is used in large number of diseases such as headache, arthralgia cases where mild analgesic treatment is required. A number of methods of its determination are suggested in the literature. It is a well-known non-selective COX (cyclooxygenase) inhibitor [1], but its medical use may be associated with a variety of side effects [2–7]. Formerly, the oxidation of aspirin with a number of oxidants like potassium bromate [8], N-bromoacetamide [9], N-bromosuccinimide [10] was studied in several works.

Hexacyanoferrate (III) (HCF (III)) serves as a one-electron oxidant with a redox potential of 0.36 V, functioning as a proton or electron abstracting reagent in oxidation reactions [11, 12]. A plethora of redox reactions, involving compounds such as paracetamol, sulfanilic acid, crotyl alcohol, formazans, and ascorbic acid, have been conducted in alkaline media, both with and without catalysts. HCF (III) finds application in the oxidimetric determination of organic and inorganic compounds in both acidic and alkaline environments. Although its utilization in acidic media is limited due to complexation between the oxidized and reduced products of HCF (III), reactions in alkaline media exhibit reduced susceptibility to this complication. However, they generally suffer from slower kinetics attributed to the reduced oxidation potential of the $[Fe(CN)_6]^{3-}$/ $[Fe(CN)_6]^{4-}$ redox couple [13].

It has a number of applications in organic chemistry for synthesis [14-17] of newer organic compounds. The reagent attacks the substrate in one equivalent step producing a free radical [18, 19]. Such a free radical has several options such as attack by the oxidant, dimerization or polymerization, etc. The product hexacyanoferrate(II) is transparent to photo light, therefore, hexacyanoferrate(III) can be estimated spectrophotometrically [20] in the reaction system to monitor the kinetics of any reaction provided the reactants and products are colorless or do not exhibit any absorbance in the visible region. Additionally, in the presence of light, Fe $(CN)_6^{3-}$ ions hydrolyze gradually in acidic aqueous solutions, forming hydroxy- or aquo-penta cyanoferrate (III) complexes. This hydrolysis may lead to a shift in solution pH, particularly in neutral, unbuffered media.

To mitigate this challenge, various transition metal ions have been employed as catalysts in alkaline media, including osmium (VIII) [21-23], ruthenium (III) [24-26], (IV) [27], (VI) [28], and (VIII) [29], rhodium (III) [30], iridium (III) [31, 32], palladium (II) [33, 34], and molybdenum (IV) [35, 36].

Ru (III) acts as a catalyst in the oxidation of many organic and inorganic substrates [37, 38]. The production of many intermediary complexes and distinct oxidation states of ruthenium (III) might make the catalyzed mechanism extremely complex.

* To whom all correspondence should be sent:
E-mail: *l.p_riya@yahoo.co.in*

Although catalysis by transition metal ions depends on the nature of the substrate, oxidant, and experimental conditions, it has been reported that metal ions act as catalysts [39, 40] by one of several different paths, such as formation of complexes with reactants, oxidation of the substrate itself or through the formation of free radicals. Ruthenium (III) chloride has been used in several redox reactions particularly in acidic medium [41-43] as it is known to be an efficient, non-toxic and homogeneous catalyst.

Investigating the complexation events and reactivity patterns between aspirin and oxidants under varied reaction settings, as well as connecting kinetic concepts with thermodynamic viewpoints, are the main goals of this work. When comparing the characteristics of a variety of frequently observed reactions and deciphering reaction mechanisms, these metrics are essential.

EXPERIMENTAL

Materials and methods

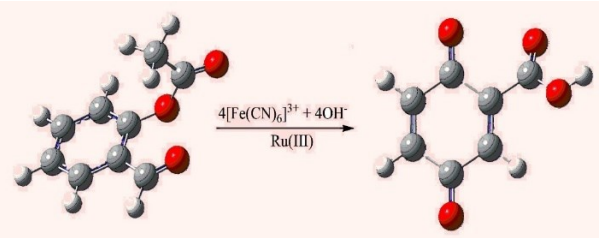
Aspirin was used exactly as prescribed, with no additional care. Double-distilled water was used to make an aspirin stock solution kept at room temperature. In this investigation, AnalaR grade reaction components were used. The necessary amount of hexacyanoferrate (III) and ruthenium (III) chloride was dissolved in double-distilled water to create the solutions. The oxidant and catalyst solution was maintained in a black painted bottle and kept in a refrigerator at ~5 ˚C.

Kinetic procedure

Until otherwise noted, the reactions were carried out in glass stoppered Erlenmeyer flasks that were suspended in a water bath thermostated at ±0.1 °C and had a black coating on the outside. The time of initiation was recorded when half of the pipette's contents were discharged into the reaction mixture. The reactions were started by adding temperature-equilibrated solutions of hexacyanoferrate (III). An aliquot (5 cm^3) of the reaction mixture was periodically removed to observe the kinetics spectrophotometrically [42] at λ_{max} 420 nm (ε=1020 dm^3 mol^{-1} cm^{-1}) after the reaction mixture had been well agitated. In triplicate, the results were shown to be reproducible within ± 5 %.

Stoichiometry

The excess of HCF(III) over aspirin was used to study the reaction's stoichiometry. After completion, the reaction shows that four moles of HCF(III) are needed for every mole of aspirin. The quinone form is also confirmed by the color signal, therefore the reaction's stoichiometry matches the one shown in the following scheme:



RESULTS AND DISCUSSION

Hexacyanoferrate(III) concentration dependence

While maintaining constant concentrations of the other reaction ingredients, namely aspirin [ASP] = 1.0×10^{-2} mol dm^{-3} and [Ru(III)] = 1.0×10^{-4} mol dm^{-3} at 45 °C under pseudo first order conditions, the concentration of hexacyanoferrate(III) [HCF(III)] was varied from 3.0×10^{-4} to 10.0×10^{-4} mol dm^{-3} at two fixed concentrations of [OH^-] = 0.05 and 0.075 mol dm^{-3}, respectively. Log [HCF(III)]t *vs* time was plotted in pseudo first order, and pseudo first order rate constants k (s^{-1}) were computed. The conforming order with regard to the oxidant was determined to be one, and the first order rate constants were found to be independent of the gross starting concentrations of HCF(III) (Fig.1).

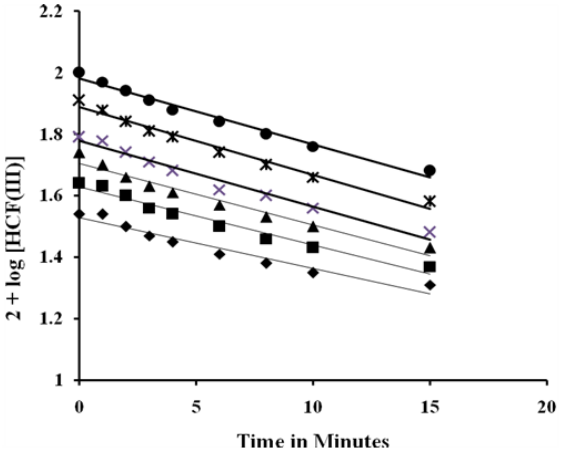


Fig. 1. Pseudo first order plots of HCF(III). [HCF(III)] = (1) ♦ 3.0×10^{-4}; (2) ■ 4.0×10^{-4}; (3) ▲ 5.0×10^{-4}; (4) × 6.0×10^{-4}; (5) ✳ 8.0×10^{-4}; (6) ● 10.0×10^{-4}; [ASP] = 1.0×10^{-2} mol dm^{-3}; [OH^-] = 0.05 mol dm^{-3} ; [Ru(III) = 1.0×10^{-4} mol dm^{-3}; 45 °C

Aspirin dependence

At four different temperatures (35, 40, 45, and 50 °C, respectively) and with constant concentrations of the remaining reaction ingredients ([HCF(III)] = 5.0×10^{-4} mol dm^{-3}; [OH^-] = 0.075 mol dm^{-3}; and [Ru (III)] = 1.0×10^{-4} mol dm^{-3}), the aspirin concentration was adjusted from 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3} (Fig. 2). Plots of pseudo first order were created. Plotting the

pseudo first order rate constant *vs* [ASP] shows that at lower aspirin concentrations, the order is one; at higher aspirin concentrations, however, the rate tends to a limiting value. Such a pattern of aspirin concentration change suggests that the aspirin order is complicated. Additional tests were carried out at two additional hydroxide ion concentrations, 0.05 and 0.1 mol dm^{-3}, to confirm this.

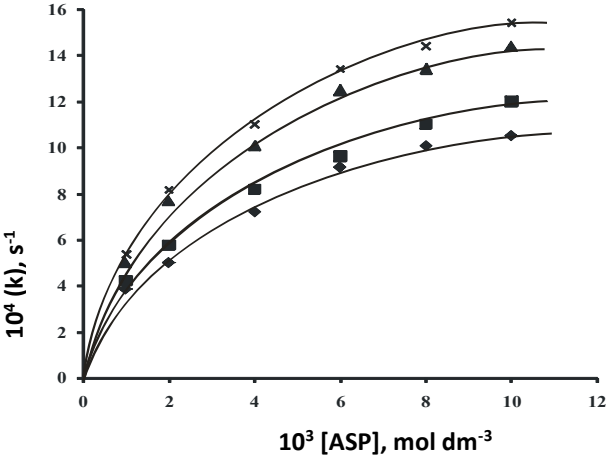


Fig. 2. Variation of aspirin at different temperatures. [HCF(III)] = 5.0×10^{-4} mol dm^{-3}; [OH^-] = 0.075 mol dm^{-3}; [Ru(III)] = 1.0×10^{-4} mol dm^{-3} Temperature ♦ 35, ■40, ▲45 and × 50 °C

Ru (III) dependence

At a given concentration of other reaction components, such as [HCF(III)] = 5.0×10^{-4} mol dm^{-3}, [ASP] = 1.0×10^{-2} mol dm^{-3}, and [OH^-] = 0.05 mol dm^{-3} at 45 °C, the concentration of [Ru (III)] was changed from 1.0×10^{-5} to 8.0×10^{-5} mol dm^{-3}. The rate rises as the concentration of [Ru (III)] increases. A straight line through the origin of a plot of the pseudo first order rate constant *v/s* [Ru (III)] showed first order dependency on the catalyst. Further confirmation of this dependence was obtained at [OH^-] = 0.075 mol dm^{-3}.

Hydroxıde ıon dependence

With the concentrations of the other reaction ingredients, namely [ASP] = 1.0×10^{-2} mol dm^{-3}, [Ru (III)] = 1.0×10^{-4} mol dm^{-3}, [I] = 0.1 mol dm^{-3}, and [HCF(III)] = 5.0×10^{-4} mol dm^{-3}, held constant, the concentration of the hydroxide ion was adjusted from 4.0×10^{-2} mol dm^{-3} to 10.0×10^{-2} mol dm^{-3} at 45 °C (ionic strength was maintained by employing sodium nitrate). The rate first rises as the hydroxide ion concentration increases, but at higher hydroxide ion concentrations, it reaches a limiting value. By conducting the reaction at two additional temperatures, such as 40 and 50 °C, respectively, this was further verified. This demonstrates how the rate changes intricately with the concentration of hydroxide ions.

Effect of ıonıc strength (ı)

By altering the concentration of $NaNO_3$ while maintaining constant concentrations of the other reaction ingredients; [ASP] = 1.0×10^{-2} mol dm^{-3}, [OH^-] = 0.075 mol dm^{-3}, [Ru (III)] = 1.0×10^{-4} mol dm^{-3}, and [HCF(III)] = 5.0×10^{-4} mol dm^{-3} at 45 °C; the impact of ionic strength was investigated. As the concentration of $NaNO_3$ rises, so does the rate.

Effect of temperature

While maintaining constant concentrations of the other reaction ingredients, namely [HCF(III)] = 5.0×10^{-4} mol dm^{-3}, [Ru (III)] = 1.0×10^{-4} mol dm^{-2}, and [I] = 0.075 mol dm^{-3}, the impact of temperature on the pace of reaction was also investigated at 35, 40, 45, and 50 °C, respectively. The Eyring equation {ln k/T v/s 1/T} was utilized to assess the activation characteristics, including energy and entropy of activation. According to the calculations, the activation energy was 15.7 ± 0.06 kJ mol^{-1} and the entropy was -171.98 ± 0.22 JK^{-1} mol^{-1}.

Test of free radıcals

Free radicals were tested by adding acrylic acid monomer into the reaction mixture, no white ppt was observed for a longer time. A free radical should be formed in view of one equivalent nature of the oxidant. It appears that the radical is formed in the solvent cage and immediately reacts without diffusing out of the cage to interact with the monomer. Probably, it is this reason that the monomer is not polymerised and no visible polymer was obtained.

Effect of hexacyanoferrate (ıı)

HCF(II), one of the reaction products, is without any effect on the rate of the reaction and even after three half-lives does not indicate deviations from first order. Also, addition of hexacyanoferrate(II) does not indicate any effect, such as observation is important in light of the fact that any equilibrium involving HCF(II) preceding the rate determining step is not involved.

Mechanısm of oxıdatıon

The catalyst $RuCl_3$ (1×10^{-5} mol dm^{-3}) in the range of (1×10^{-3} - 1×10^{-4}) mol dm^{-3} exhibits [44, 45] various types of hydroxo-aquo ruthenium (III) chloride complexes governed by equilibria (1) to (3) as follows:

$$[Ru(H_2O)_6^{3+}] + OH^- \overset{K_1}{\rightleftharpoons} [Ru(H_2O)_5OH]^{2+} \quad (1)$$

$$[Ru(H_2O)_5OH]^{2+} + OH^- \underset{}{\overset{K_2}{\rightleftharpoons}} [Ru(H_2O)_4(OH)_2]^+ \quad (2)$$

$$[Ru(H_2O)_4(OH)_2]^+ + OH^- \underset{}{\overset{K_3}{\rightleftharpoons}} [Ru(H_2O)_3(OH)_3] \quad (3)$$

Hence, no evidence for an oxo-bridged complex between catalyst and substrate was observed kinetically to account for complex dependence of the substrate and hydroxide ion respectively.

The hydroxide ion concentration range employed in the reaction (< 10^{-2} mol dm^{-3}) ascribes the reactive form of [Ru $(H_2O)_6^{3+}$] to be [Ru $(H_2O)_5OH]^{2+}$. Thus, considering Fe $(CN)_6^{3-}$, ASP (ASP has been written heretofore for aspirin and [Ru $(H_2O)_5OH]^{2+}$ to be the reactive forms of hexacyanoferrate (III), aspirin and ruthenium (III) chloride respectively, the following reaction mechanism can be proposed.

$$Ru^{III}(H_2O)_6]^{3+} + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Ru^{III}(H_2O)_5OH]^{2+} + H_2O \quad (4)$$

$$Ru^{III}(H_2O)_5OH]^{2+} + ASP \underset{}{\overset{K_2'}{\rightleftharpoons}} [Ru^{III}(H_2O)_5OH.ASP]^{2+} \quad (5)$$

$$[Ru^{III}(H_2O)_5OH.ASP]^{2+} + Fe(CN)_6^{3-} \xrightarrow[k]{Slow} [Ru^{IV}(H_2O)_5OH.ASP]^{3+} + Fe(CN)_6^{4-} \quad (6)$$

$$Ru^{IV}(H_2O)_5OH.ASP]^{3+} + Fe(CN)_6^{3-} \xrightarrow{Fast} [Ru^{V}(H_2O)_5OH.ASP]^{4+} + Fe(CN)_6^{4-} \quad (7)$$

$$Ru^{V}(H_2O)_5OH.ASP]^{4+} \xrightarrow{Fast} Int. + [Ru^{III}(H_2O)OH]^{2+}$$

$$Int. + 2Fe(CN)_6^{3-} \longrightarrow Products + 2Fe(CN)_6^{4-} \quad (8)$$

Such a mechanism leads to the rate law (9):

$$\frac{-d[Fe(CN)_6^{3-}]}{dt} = \frac{kK_1K_2'[Fe(CN)_6^{3-}][Ru(H_2O)_6^{3+}][ASP][OH^-]}{1+K_1[OH^-]+K_1K_2'[OH^-][ASP]} \quad (9)$$

where [$Fe(CN)_6^{3-}$] and [$Ru^{(III)}$] are the gross analytical concentrations of hexacyanoferrate(III) and ruthenium(III) respectively. [ASP] is the free equilibrium concentration of aspirin.

The rate law (9) is re-written as (10):

$$k' = \frac{kK_1K_2'[ASP][OH^-]}{1+K_1[OH^-]+K_1K_2'[ASP][OH^-]} \quad (10)$$

where k′ is an observed second order rate constant. The double reciprocal of eqn (10) yields eqn (11)

$$1/k' = \frac{(1+K_1[OH^-])}{kK_1K_2'[ASP][OH^-]} + \frac{K_1K_2'[ASP][OH^-]}{kK_1K_2'[ASP][OH^-]}$$

$$= \frac{(1+K_1[OH^-])}{kK_1K_2'[ASP][OH^-]} + \frac{1}{k} \quad (11)$$

A plot of 1/k′ *versus* 1/[ASP] was made from eqn (11) that yielded a straight line with non-zero intercept (Fig. 3). The slope of the line is given by eqn (12):

$$Slope = \frac{1+K_1[OH^-]}{kK_1K_2'[OH^-]} = \frac{1}{kK_1K_2'[OH^-]} + \frac{K_1[OH^-]}{kK_1K_2'[OH^-]}$$

$$= \frac{1}{kK_1K_2'[OH]} + \frac{1}{kK_2'} \quad (12)$$

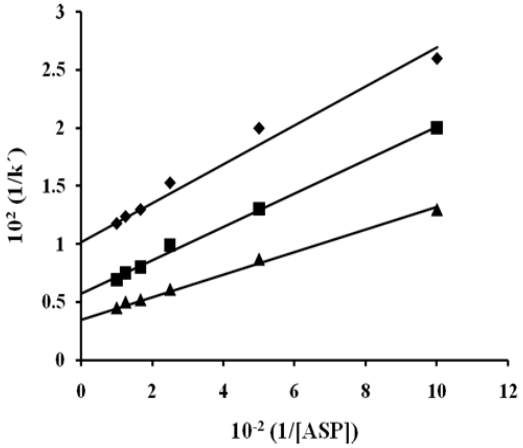


Fig. 3. Plot of 1/k′ versus 1/[ASP].
[HCF(III)] = 5.0 × 10^{-4} mol dm^{-3}; [Ru(III)] = 1.0 × 10^{-4} mol dm^{-3}; [OH^-] = ♦ 0.05, ■ 0.075, ▲ 0.1 mol dm^{-3} and 45 °C

A further plot of slope *versus* $[OH^-]^{-1}$ was made from eqn (12) that also yielded a straight line with non-zero intercept (Fig. 4).

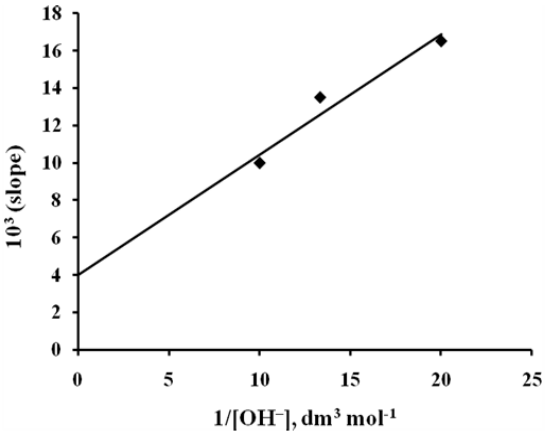


Fig. 4. Plot of slope *versus* 1/[OH^-].
[HCF(III)] = 5.0 × 10^{-4} mol dm^{-3}; [ASP] = 1.0×10^{-3} - 1.0×10^{-2} dm^{-3}; [Ru(III)] = 1.0 × 10^{-4} mol dm^{-3} and 45 °C

At 45 °C, 'K_1' was determined to be 6.15 based on the intercept-to-slope ratio. Using 'k' determined from Fig. 3, K_2' was computed from the intercept to be 25.51, 14.25, and 8.75 dm^3 mol^{-1} s^{-1} at I=0.05, 0.075, and 0.1 mol dm^{-3}, respectively. A plot of $(k')^-$

^{1} *vs* $(ASP)^{-1}$ at various temperatures, such as 14.28, 16.13, 17.86, and 20.0 s^{-1} at 35, 40, 45, and 50 °C, respectively, was used to compute 'k' from Fig. 5. I = 0.075 mol dm^{-3} was also used.

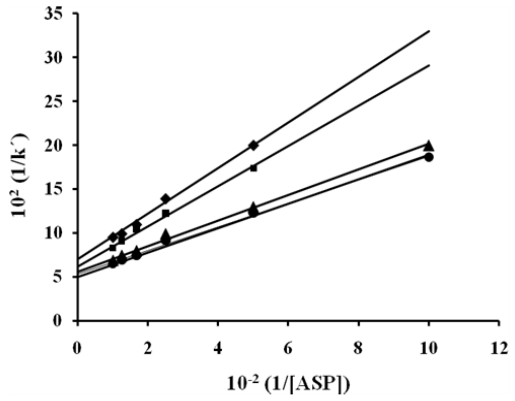


Fig. 5. Plot of 1/k′ *versus* 1/[ASP].
[HCF(III)] = 5.0 × 10^{-4} mol dm^{-3}; [Ru(III)] = 1.0 × 10^{-4} mol dm^{-3}; [OH^{-}] = 0.075 mol dm^{-3} Temperatures = ♦ 35, ■ 40, ▲ 45 and ● 50 °C

The energy and entropy of activation employing rate constant (k_1) for the rate determining step to be 15.7±0.06 kJ mol^{-1} and -171.98±0.22JK^{-1} mol^{-1} respectively employing Eyring equation.

Thus, in the light of the mechanism proposed for the title reaction that accounts for all experimental observations, the reaction scheme-I can be suggested for the transfer of electrons from the substrate to the oxidant.

Not much is known about alkaline chemistry of aspirin. The likely species of this reagent is in anionic form in alkaline medium. The rate depends upon hydroxide ion concentration in a complex manner. This shows that hydroxide ion is also involved in activated complex along with aspirin and hexacyanoferrate (III). The reaction is catalyzed by ruthenium (III) chloride. So far, there is no report of any reaction between Fe $(CN)_6^{3-}$ and hydroxide ion, the involvement of the latter in the activated complex appears through the reactive form of the catalyst. The kinetic order with respect to the oxidant is one whereas a complex order is indicated by the substrate.

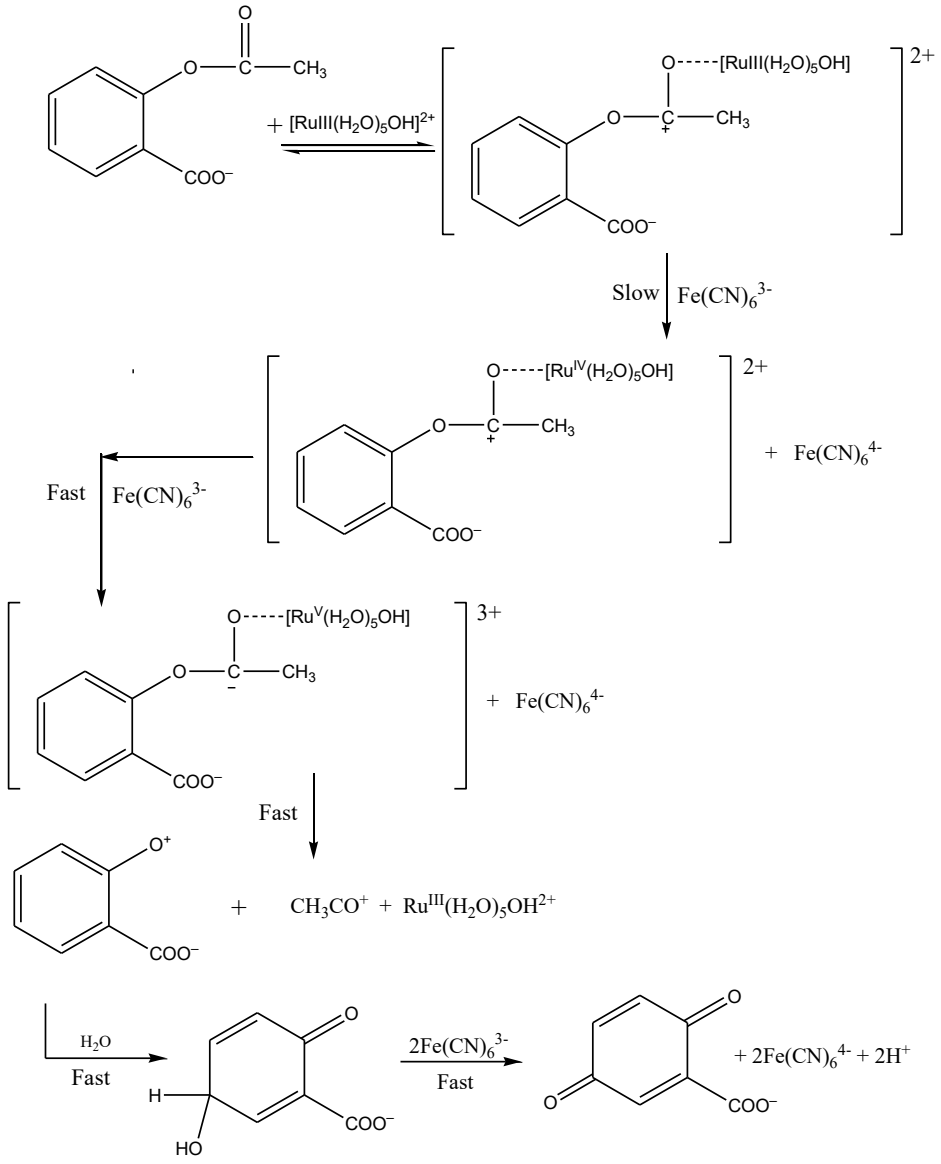
K^{+} and [Fe $(CN)_6^{3-}$] ion pairing is reported [46] earlier but no such ion pairing is known in case of Na^{+} and Fe $(CN)_6^{3-}$. Probably it is due to the fact that ion association decreases with increasing size of the cation [47]. Since a large concentration of sodium ions is present in the reaction system, the probability of ion-pairing between Na^{+} and [Fe $(CN)_6^{3-}$] cannot be completely ruled out. The rate of the reaction increases with increasing ionic strength, such an increase in rate cannot be assigned to interaction of unlike charged species in the rate controlling step of the reaction mechanism despite ion association of [Fe $(CN)_6^{3-}$] and Na^{+}. However, an increase in rate owing to ionic strength for six-fold variation increases rate by almost two-fold.

The variation in ionic strength does not hold good for Davies equation [48], an increase in rate with increasing ionic strength cannot be inferred even qualitatively as the reaction is between differently charged species. If it is assumed that the ion-pair such as Na^{+} $[Fe(CN)_6]^{3-}$ is more reactive than simple ionic species such as [Fe $(CN)_6^{3-}$], such a small increase in rate due to large ionic strength can be accounted for decrease in electrostatic repulsion. Specific ionic effects [49] are simply found in the presence of large concentrations of the cations, it appears that such a tendency in the title reaction is either marked by the rate dependence on hydroxide ion concentration or is absent at all.

CONCLUSION

According to the kinetic data, the order with regard to the oxidant and the catalyst, respectively, is one, whereas the reaction kinetics show a complicated dependence of the hydroxide ion and aspirin. The reaction's stoichiometry is 1:4, meaning that four moles of HCF (III) are needed for every mole of substrate. In conclusion, we believe that the likelihood of an intermediate complex forming between the oxidant and the substrate is minimal, at least when considering substitutionally inert HCF (III) under milder circumstances used in our studies. Additionally, the complexation between the catalyst and the substrate makes sense because it implies that product HCF (II) has no influence. This is significant because there is no equilibrium involving HCF(II) prior to the rate-determining step.

Acknowledgement: *R. Sailani expresses gratitude to the Department of Chemistry at the University of Rajasthan in Jaipur, Rajasthan, India, as well as her co-authors. The University Grant Commission in New Delhi, India, provided financial assistance for this work in part through the JRF. This paper is dedicated by the author, R. Sailani, to Prof. (Late) P. D. Sharma of the Chemistry Department of the University of Rajasthan in Jaipur, India*



$$CH_3CO^+ + H_2O \xrightarrow{\text{Fast}} CH_3COOH + H^+$$
$$CH_3COOH + OH^- \xrightarrow{\text{Fast}} CH_3COO^- + H_2O$$
$$2H^+ + 2OH^- \xrightarrow{\text{Fast}} 2H_2O$$

Scheme I

REFERENCES

1. T. O. Cheng, *Texas Heart Inst. J.,* **34**, 392 (2007).
2. S. H. Ferreira, S. Moncada and J. R. Vane, *Braz. J. Pharmacol.*, **49**, 86 (1973).
3. H. D. Lewis, J. W. Davis, D. G. Archibald, W. E. Steinke, T. C. Smitherman, J. E. Doherty, H. W. Schnaper, M. M.LeWinter, E. Linares, J. M. Pouget, S. C. Sabharwal, E. Chesler, H. DeMots, *New Eng. J. Med.,* **309,** 396 (1983).
4. C. N. Floyd and A. Ferro, *Pharmacol. Ther.,* **141**, 69 (2014).
5. C. F. Gerhardt, *Justus Liebigs Annalen Chemie,* **87**, 149 (1853).
6. Chemical Heritage Foundation. http://www.chemheritage.org/discover/online-resources/chemistry-history/themes/pharmaceuticals/relievingsymptoms/hoffmann.aspx. Accessed 2014.
7. K. Trnavsky, M. Zachar, *Agents and Actions,* **5**, 549 (1975).
8. S. Srivastava, S. Singh, *Oxidn. Commun.*, **27**, 463 (2004).
9. A. K. Singh, A. Singh, R. Gupta, M. Saxena, B. Singh, *Trans. Met. Chem.*, **17**, 413 (1992).
10. S. Mavalang, K. Nirmal, N. Halligudi, S. T. Nandibewoor, *React. Kinet. Catal. Lett.,* **27**, 391 (2001).

11. A. I. Vovk, I. V. Muraveva, V. P. Kukhar, V. F. Baklan, *Russ. J. Gen. Chem.,* **70** 1108 (2000).
12. P.T. Speakman, W. A. Waters, *J. Chem. Soc.,* 40 (1955).
13. M. Sharma, G. Sharma, B. Agarwal, C.L. Khandelwal, P.D. Sharma, *Trans. Mat. Chem.*, **30,** 546 (2005).
14. S.K. Rajput, A. Sharma, K.N. Bapat, *Acta Ciencia Indica*, **34,** 115 (2008).
15. J.M. Leal, P.L. Domingo, B. Garcia, S. Ibeas, *J. Chem. Soc.*, *Faraday Trans.*, **89**, 3571 (1993).
16. V.N. Singh, M.C. Gangwar, B.B. Saxena, M.P. Singh, *Can. J. Chem*, **47,** 1051 (1969).
17. V.N. Sigh, M.P. Singh, B.B. Saxena, *Ind. J. Chem.*, **8**, 529 (1970).
18. M. Martinez, M. Pitarque, R.V. Eldik, *J. Chem. Soc. Dalton Trans.*, 2665 (1996).
19. E.P. Kelson, P.P. Phengsy, *Int. J. Chem. Kinet.*, **32**, 760 (2000).
20. K. Wilson, J. Walker, *J. Practical Biochemistry*, 5th ed. Cambridge University Press, (2005).
21. S. A. Farokhi, S. T. Nandibewoor, *Catal. Lett.,* **129**, 207 (2009).
22. S. Dubey, N. Sharma, C. L. Khandelwal, *Trans. Met. Chem.,* **28**, 176 (2003).
23. P. Sharma, R. Sailani, A. Meena, C. L. Khandelwal, *J. Chem. Res.* **44**, 295 (2020).
24. R.M. Naik, A. Srivastava, A. K. Verma, *Turk. J. Chem.,* **32**, 495 (2008).
25. R. M. Mulla, G. C. Hiremath, S. T. Nandibewoor, *Monatsh. Fur. Chem.*, **135**, 1489 (2004).
26. A. Rolaniya, A. Yadav, P. Jain, R. Sailani, *ChemistrySelect,* **9**, e202303734 (2024).
27. E. P. Kelson, P. P. Phengy*, Int. J. Chem. Kinet.,* **32**, 760 (2000).
28. A. Mucients, F. J. Poblete, D. Rodriguez, *Int. J. Chem. Kinet.,* **31**, 1 (1999).
29. K.P. Tandon, A. K. Singh, R. Baboo, *Oxidn. Commun.,* **28**, 611 (2005).
30. B. Prasad, R. P. Singh, *Aryabhata. Res. J. Phy. Sci.,* **6**, 127 (2003).
31. S. K. Rajput, A. Sharma, K. N. Bapat, *Acta. Cien. Ind. Chem.,* **34**, 115 (2008).
32. A. Goel, R. Sharma, *J. Chem. Eng. Mat. Sci*., **31,** 1 (2012).
33. D. S. Rana and P. C. Mathur, *J. Ind. Coun. Chem.,* **10**, 33 (1994).
34. A. Fawzy, *J. Chem. Sci*., **128**, 247 (2016).
35. Ahmad, C. M. Ashraf, *Ind. J. Chem*., **17A**, 302 (1979).
36. J. C. Swarts, C. R. Dennis, S. B. Stephen, *Reac. Kinet. Mech. Catal.,* **137**, 1 (2023).
37. R. M. Naik, A. Srivastava, A. K. Verma, *Turk. J. Chem*., **32**, 495 (2008).
38. Mulla, R. M.; Hiremath, G. C. Nandibewoor, S. T. *Monatsh. Fur. Chem*., **135**, 1489 (2004).
39. S. A. Chimatadar, A. K. Kini S. T. Nandibewoor, *Bioinorg. React. Mech.,* **5(3)**, 231 (2005).
40. A. K. Singh, S. Rahmani, B. Singh, R. K. Singh M. Singh, *J. Phys. Org. Chem*., **17(3)**, 249 (2004).
41. P.A. Prashanth, S. Ananda, K. S. Rangappa M. N.Kumara, *J. Mol. Cat. A: Chem.*, **383**, 203 (2014).
42. A. A. P. Khan, A. Khan, A. M. Asiri A. K. Singh, *Int. J. Electrochem. Sci.*, **10(1)**, 759 (2015).
43. R. V. Nadh, B. S. Sundar P. S. Radhakrishnamurti, *Rus. J. Phys. Chem. A*, **90**, 1760 (2016).
44. A.E. Mucientes, F.J. Poblete, R.E. Gabaldon, A.M. Rodriguez F. Santiago, *J. Chem. Res.(s)*, **286**, 1324 (1998).
45. W. Bottcher, G.M. Brown and N. Sutin, *Inorg. Chem.*, **18**, 1447 (1979).
46. S. J. Paton C.H. Brubaker, *J. Inorg. Chem.*, **12**, 402 (1973).
47. D. Mohan, V.K. Chhabra Y.K. Gupta, *J. Chem. Soc., Dalton. Trans.*, 1737 (1975).
48. C.W. Davies, Ion Association, Butter Norths, London, 1962.
49. Y.A. Mazid K.E. Howlett., *J. Chem. Soc.(A),* 679 (1968)