



KINETICS AND MECHANISM OF REDUCTION OF [(Fe(SALOPH))₂-μ-DICARPY] COMPLEX BY L-ASCORBIC ACID IN ACID MEDIUM



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Received: December 23, 2017

Accepted: February 28, 2018

Abstract: The kinetics and mechanism of the reduction of iron(III) dimer, [(Fe(saloph))₂-μ-dicarpy] by L-ascorbic acid (H₂A), in perchloric acid has been studied spectrophotometrically at λ_{max} = 424 nm. The stoichiometric studies showed that 1 mole of H₂A is oxidized for every mole of [(Fe(saloph))₂-μ-dicarpy] reduced. Under pseudo-first order conditions of concentrations of [H₂A] >> [(Fe(saloph))₂-μ-dicarpy], the order with respect to [(Fe(saloph))₂-μ-dicarpy] is unity and half-order with respect to H₂A as plot of logk_{obs} versus log[reductant] showed linearity to about 85% extent of reaction. Second order rate constant (k₂) were determined as the ratio of k_{obs} to [H₂A] and was found to be fairly constant. Reaction rate was inversely dependent on acid concentration and rate increased with increase in ionic strength of reaction system. Also, increase in dielectric constant of the reaction medium (D) decreased rate of reaction and addition of CH₃COO⁻, SO₄²⁻, NO₃⁻ or Cl⁻ catalyzed the rate of reaction. Activation parameters evaluated gave E_a = 14.805, ΔH^{*} = 12.122 kJmol⁻¹ and ΔS^{*} = -268.86 JK⁻¹mol⁻¹. The rates are consistent with mechanism involving the formation of free radicals and precursor complex prior to electron transfer. Michaelis-Menten plot of 1/k_{obs} versus 1/[reductant] was linear with positive intercept for the system. The rate law is given as; $\frac{-d[\text{Fe}_{2-\mu\text{-dicarpy}}^{4+}]}{dt} = (k_3 + K_a K_1 k_1 [\text{H}^+]^{-1}) [\text{Fe}_{2-\mu\text{-dicarpy}}^{4+}] [\text{H}_2\text{A}]$. The reduction of [(Fe(saloph))₂-μ-dicarpy] by H₂A is rationalized in terms of ion-pair complex formation with outer sphere character.

Keywords: Iron(III) dimer, kinetics, L-ascorbic acid, mechanism, reduction, saloph

Introduction

Many studies had been devoted to the chemistry of iron and its compounds mainly due to its physiological applications in biological systems. Iron-saloph complexes exhibit interesting structural, catalytical, electronic, optical, magnetic and bio-active properties (Kennedy *et al.*, 1987; Dusek *et al.*, 1992; Prakash *et al.*, 2011; Atiga *et al.*, 2015). Complexes of the composition [Fe(saloph)₂L] with L = 2,5-pyridinedicarboxylic acid, acetylenedicarboxylic acid and 1,3,5-benzenetricarboxylic acid (Kopel *et al.*, 1998) and other derivatives has been synthesized and characterized. The properties of the μ-oxo-bridged iron complexes, [{Fe(salen)}₂O] (salenH₂ = N,N'-bis(salicylidene) ethylenediamine) and [{Fe(saloph)}₂O] (salophH₂ = bis(salicylidene)-o-phenylenediamine), and their properties and X-ray studies are mentioned in many works (Ashmawy *et al.*, 1991; Kopel *et al.*, 1998).

Recent interest in the studies of the electron transfer reactions of salen and saloph iron(III) bridged complexes have increased greatly. This could revolve around their resemblance to porphyrins and also to enhance understanding of their biomimetic action mode of closely related complexes in biological systems.

The electron transfer reactions of dinuclear iron(III) ion, [Fe₂O]⁴⁺, with L-ascorbic acid (Ukoha and Iyun, 2002), have been reported. Interest in the reactions of L-ascorbic acid continues to be keen and has caught the attention of researchers. Due principally to its major role as an antioxidant and other physiological significance (Birch and Parket, 1974), numerous studies on its oxidation by transition metal complexes had been undertaken. Its electron transfer reactions with iron(III) complex, hexacyanoferrate(III) has been reported and an outer-sphere electron transfer has been proposed as its mechanistic pathway (Leal *et al.*, 1993).

Oxo-bridged, μ-bipyridyl-bridged, salen-bridged, μ-adipic acid-bridged iron(III) complexes has been synthesized,

characterized and kinetic data documented as regards their electron transfer behaviour with L-ascorbic acid and thiols (Ukoha and Iyun, 2002; Alioke *et al.*, 2012; Atiga *et al.*, 2013). Apart from reported work on the synthesis and characterization of [(Fe(saloph))₂-μ-dicarpy] (Kopel *et al.*, 1998), there is no documented work on the electron transfer reactions of the iron(III) dimer, [(Fe(saloph))₂-μ-dicarpy]. Therefore, there is need to carry out kinetic investigations on this dimer and develop mechanisms for their electron transfer behaviour with reducing agents as information gathered will add to knowledge and enhance understanding as to the action mode of related complexes in biological systems.

Materials and Methods

Preparation of N,N'-bis(salicylidene)-o-phenylenediamine (saloph)

N, N'-bis(salicylidene)-o-phenylenediamine hereafter referred as saloph, was prepared, purified and characterized following the methods of Liu *et al.*, (2007) with little modification. The reaction occurs in the ratio of 2:1 (salicylaldehyde : o-phenylenediamine). Salicylaldehyde (0.1 mole, 10.47 cm³) was transferred into a reflux flask and 0.05 mole (5.407 g) of o-phenylenediamine dissolved in 25 cm³ ethanol was added. This was gradually poured into the reflux flask and more solvent added. The mixture was refluxed for 2.5 h at 50°C. It was cooled, the precipitate collected by filtration, washed with ethanol and recrystallized using 3: 1 (ethanol:DMSO) mixture. The crystals were later filtered and air dried at room temperature.

Preparation of [{Fe(saloph)}₂(2,5-pyridine dicarboxylic acid)] [(Fe(saloph))₂(2,5-pyridinedicarboxylic acid)] hereafter denoted as [(Fe(saloph))₂(2,5-dicarpy)] was prepared, purified and characterized following the method of Kopel *et al.* (1998). Firstly, [(Fe(saloph))₂O] was prepared by adding concentrated solution of NH₄OH to stirred hot ethanol solution of Fe(saloph)Cl in a beaker until it was alkaline (pH 10.02). The

alkalinity was measured with a PHS-25 Precision pH meter (Lida Instrument) which was calibrated before use. $[(\text{Fe}(\text{saloph})_2\text{O})]$ (1 mmol (0.7644 g) was suspended into hot butanol (40 cm³) in a reflux flask and solution of 2,5-pyridine dicarboxylic acid (0.1 g, 0.6 mmol) in butanol (10 cm³) was added while stirring it. The reaction mixture was then boiled under reflux for 3 h, cooled, the precipitate filtered, washed with butanol and dried with anhydrous Na₂SO₄ for 24 h.

Preparation of standard solutions

$[(\text{Fe}(\text{saloph})_2(2,5\text{-dicarpy}))]$

$[(\text{Fe}(\text{saloph})_2(2,5\text{-dicarpy}))]$ (oxidant) was prepared by dissolving 0.0018 g of the synthesized product in 2 cm³ dimethylsulphoxide (DMSO) to make a stock solution of 0.001 mole dm⁻³. Fresh solutions were prepared daily for the kinetic studies.

L-ascorbic acid hereafter denoted as H₂A and all other reagents were of analytical grade and were used as supplied. Standard solutions were prepared in deionised water and 75-Series Single beam UV-Visible spectrophotometer was used in recording absorbances of solutions.

Kinetic measurements

The rate of reaction of the iron(III) dimer with H₂A was studied by monitoring the decrease in the absorbance of the complex at 424 nm in which all other species in the reaction medium at this wavelength were found to have any significant interference. Kinetic measurements were carried out under pseudo-first order conditions, with H₂A in at least 100 fold excess over the oxidant by following the rate of change of absorbance of the reaction mixture. Ionic strength, I = 1.0 x 10⁻³ mole dm⁻³ (NaClO₄) as well as the hydrogen ion concentrations, [H⁺] = 1.0 x 10⁻⁴ mole dm⁻³ of the medium was maintained constant at 29.0°C. Under such conditions, kinetic curves were exponential and rate constant obtained from logarithmic plot of the absorbance differences $\ln(A_t - A_\infty)$ versus time and the slope gave the pseudo-first order rate constant based on the relation in Equation (1).

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_{\text{obs}}t \dots\dots\dots(1)$$

where: A_t and A_∞ represents the absorbances at time 't' and infinity respectively and k_{obs} is pseudo-first order rate constant.

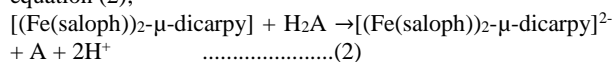
Spectrophotometric titration was used to determine the stoichiometry of the oxidation of L-ascorbic acid by $[(\text{Fe}(\text{saloph})_2(2,5\text{-dicarpy}))]$. The final absorbance, A_∞, were measured at 424 nm for series of solutions containing a constant concentration of iron(III) dimer, [H⁺], ionic strength and varied concentrations of H₂A between 1.0 x 10⁻⁵ – 8.0 x 10⁻⁴ mole dm⁻³ at 29.0°C.

The intervention of free radicals generated during the reduction of $[(\text{Fe}(\text{saloph})_2(2,5\text{-dicarpy}))]$ by H₂A was investigated. This was detected by monitoring gel formation by adding a free radical scavenger, acrylamide, in a partially reacted reaction mixture in excess methanol.

Results and Discussion

Stoichiometry

The result from the plots of A_∞ against mole ratio (H₂A/ $[(\text{Fe}(\text{saloph})_2\text{-}\mu\text{-dicarpy})]$) of the stoichiometric studies showed that one mole of $[(\text{Fe}(\text{saloph})_2\text{-}\mu\text{-dicarpy})]$ is reduced per mole of H₂A oxidised. The results are consistent with equation (2);



(A = dehydroascorbic acid).

Some redox reactions of ascorbic acid had been reported where dehydroascorbic acid is the major organic product of the reaction. L-ascorbic acid reacts with N,N'-ethylenebis(salicylideneiminato)Mn(III) complex (Salem and Gemeay, 1996), oxo-bridged diruthenium(III), [Ru₂O]⁴⁺ (Iyun

et al., 1995), N,N'-salicylideneiminatoiron(III) complex (Alioke *et al.*, 2012) resulted in the formation of dehydroascorbic acid.

Reaction order

Under pseudo-first order conditions of [H₂A] >> $[(\text{Fe}(\text{saloph})_2\text{-}\mu\text{-dicarpy})]$, the kinetic studies done showed linearity of above 85% extent of reaction indicating first order dependence of rate on $[(\text{Fe}(\text{saloph})_2(2,5\text{-dicarpy}))]$. It also suggests no inhibition of the reaction by the products for this extent of reaction. This was obtained from the pseudo-first order plots of $\ln(A_t - A_\infty)$ versus time. The plot of log k_{obs} against log [H₂A] was linear with a slope of 0.46 (Fig. 1), indicating half order dependence of rate on [H₂A]. Second order rate constants, k₂, were determined as the ratio of k_{obs} to [H₂A] and were found to be fairly constant at 0.104 ± 0.02 dm³mol⁻¹s⁻¹ (Table 1).

Table 1: Pseudo-first order and second order rate constants for the reaction of $[(\text{Fe}(\text{saloph})_2\text{-}\mu\text{-dicarpy})]$ and L-ascorbic acid (H₂A) at $[(\text{Fe}(\text{saloph})_2\text{-}\mu\text{-dicarpy})] = 1.0 \times 10^{-5}$ mole dm⁻³, T = 29°C and λ_{max} = 424 nm

10 ³ [H ₂ A] (mole dm ⁻³)	10 ⁴ [H ⁺] (mole dm ⁻³) (HClO ₄)	10 ³ [I] (mole dm ⁻³) (NaClO ₄)	10 ⁴ k _{obs} (s ⁻¹)	k ₂ (dm ³ mole ⁻¹ s ⁻¹)
4.0	1.0	1.0	5.182	0.129
6.0	1.0	1.0	6.476	0.108
7.0	1.0	1.0	7.692	0.109
8.0	1.0	1.0	8.536	0.108
10.0	1.0	1.0	8.928	0.089
12.0	1.0	1.0	9.375	0.078

Most reactions of Fe(III) complexes with H₂A have been reported to exhibit first order dependence of rate on [H₂A] (Kimura *et al.*, 1982 replace; Ukoha, 1999). Reduction of Co(III) (Lawal, 1997) and Ru₂O⁴⁺ (Iyun *et al.*, 1995), also showed first order dependence on [H₂A].

The observed half order dependence is not so common and could point to a more complex regime of H₂A than hitherto thought of. The overall rate law can be written as equation (3) based on the above results.

$$-d[(\text{Fe}(\text{saloph}))_2 - \mu - \text{dicarpy}] / dt = k_2[(\text{Fe}(\text{saloph}))_2 - \mu - \text{dicarpy}] [\text{H}_2\text{A}]^{1/2} \dots\dots\dots(3)$$

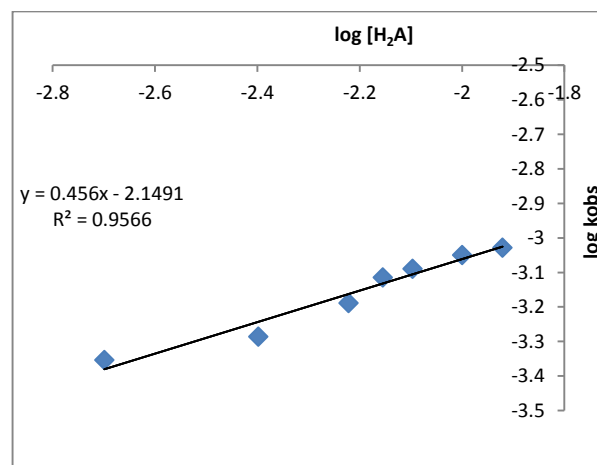


Fig. 1: Plot of log k_{obs} versus log [H₂A] for $[(\text{Fe}(\text{saloph}))_2\text{-}\mu\text{-dicarpy}]$ - H₂A Reaction

Acid dependence on reaction rate

The effect of acid concentration, [H⁺], on the $[(\text{Fe}(\text{saloph})_2\text{-}\mu\text{-dicarpy})]$ - H₂A system was investigated in the acid (HClO₄) concentration range of 1 x 10⁻⁴ ≤ [H⁺] ≤ 80 x 10⁻⁴ mole dm⁻³ while maintaining oxidant, reductant concentration and other parameters constant, showed decrease with increase in [H⁺] in

the rate of reaction as shown in Table 2. The plot of k_2 versus $\frac{1}{[H^+]}$ (Fig. 2) were linear with a positive intercept that fits into Equation (4).

$$k_2 = a + b \frac{1}{[H^+]} \dots\dots\dots(4)$$

where: $a=1.2 \times 10^{-2} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ and $b= 2.0 \times 10^{-5} \text{ s}^{-1}$ at $[H^+] = 1.0 \times 10^{-4} - 80.0 \times 10^{-4} \text{ mole dm}^{-3}$, $I = 1.0 \times 10^{-4} \text{ mole dm}^{-3}$ (NaClO_4), $[\text{H}_2\text{A}] = 10.0 \times 10^{-4} \text{ mole dm}^{-3}$, $[(\text{Fe}(\text{saloph}))_2\text{-}\mu\text{-dicarpy}] = 1.0 \times 10^{-5} \text{ mole dm}^{-3}$ and $T = 29.0^\circ\text{C}$

Table 2: Effect of $[H^+]$ on reaction rate of $[(\text{Fe}(\text{saloph}))_2\text{-}\mu\text{-dicarpy}] - (\text{H}_2\text{A})$ at $[(\text{Fe}(\text{saloph}))_2\text{-}\mu\text{-dicarpy}] = 1.0 \times 10^{-5} \text{ mole dm}^{-3}$, $T = 29^\circ\text{C}$ and $\lambda_{\text{max}} = 424 \text{ nm}$

$10^3[\text{H}_2\text{A}]$ (mole dm^{-3})	$10^4[H^+]$ (mole dm^{-3}) (HClO_4)	$10^3[I]$ (mole dm^{-3}) (NaClO_4)	10^4k_{obs} (s^{-1})	k_2 ($\text{dm}^3\text{mole}^{-1}\text{s}^{-1}$)
10.0	1.0	1.0	8.859	0.088
10.0	5.0	1.0	5.000	0.050
10.0	10.0	1.0	3.500	0.035
10.0	20.0	1.0	2.273	0.027
10.0	50.0	1.0	1.448	0.014
10.0	80.0	1.0	1.105	0.011

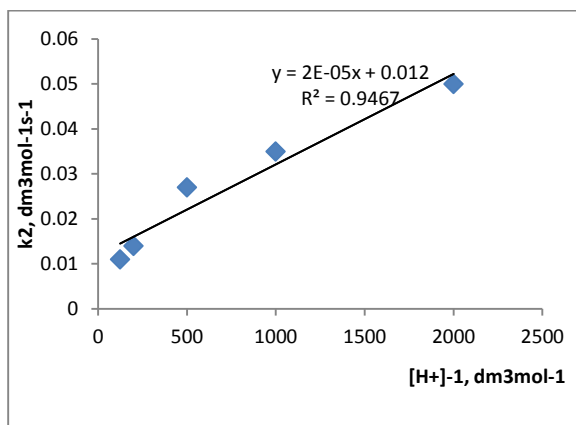
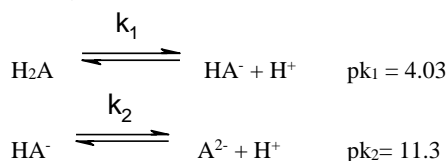


Fig. 2: Plot of k_2 versus $[H^+]^{-1}$ for the oxidation of H_2A by $[(\text{Fe}(\text{saloph}))_2\mu\text{-dicarpy}]$

This same behaviour (inverse acid dependence) had been observed for the redox reactions of H_2A with $[\text{Co}(\text{CN})_3\text{H}_2\text{O}]^{3+}$ (Dixon *et al.*, 1995), Ru_2O^{4+} (Iyun *et al.*, 1995) and Fe_2O^{4+} (Ukoha and Iyun, 2002).

The observed inverse acid dependence within the acid concentration range investigated is very much associated with a deprotonation step that occurs in most redox reactions of ascorbic acid as a structural requirement of electron transfer for H_2A . Ascorbic acid being a weak dibasic acid, dissociate with pk_1 and pk_2 of 4.03 and 11.3 respectively at 25°C (Iyun *et al.*, 1995).



H_2A species are dominant in strongly acid medium ($0 < \text{pH} < 1$), HA^- in dilute acid medium ($2.5 < \text{pH} < 5.5$) and A^{2-} species at lower acid concentration ($\text{pH} > 6$), respectively are the reactive species of ascorbic acid (Soni *et al.*, 2012).

At the range ($1.0 - 80.0 \times 10^{-4} \text{ mole dm}^{-3}$) of $[H^+]$ used and the fact that a plot of k_2 versus $[H^+]^{-1}$ was linear with intercept

suggest that H_2A and HA^- are the reactive species operating in this system.

Effect of ionic strength, dielectric constant and added anions

For $[(\text{Fe}(\text{saloph}))_2\text{-}\mu\text{-dicarpy}] - \text{ascorbic acid}$ system, ionic strength of the reaction media were varied ($1.0 - 150.0 \times 10^{-3} \text{ mole dm}^{-3}$), while maintaining other parameters constant (Table 3). Within $1.0 - 5.0 \times 10^{-3} \text{ mole dm}^{-3}$ range of ionic strength, reaction rate decreased, from $10.0 - 150.0 \times 10^{-3} \text{ mole dm}^{-3}$, there is no significant increase. The decrease from $1.0 - 5.0 \times 10^{-3} \text{ mole dm}^{-3}$ range implies interaction of cation and anion at the rate determining step while the observed decrease from $10.0 - 150.0 \times 10^{-3} \text{ mole dm}^{-3}$ is indicating interaction between cation and cation.

Table 3: Effect of varying ionic strength of the reaction medium at $[(\text{Fe}(\text{saloph}))_2\text{-}\mu\text{-dicarpy}] = 1.0 \times 10^{-5} \text{ mole dm}^{-3}$, $T = 29^\circ\text{C}$ and $\lambda_{\text{max}} = 424 \text{ nm}$

$10^3[\text{H}_2\text{A}]$ (mole dm^{-3})	$10^4[H^+]$ (mole dm^{-3}) (HClO_4)	$10^3[I]$ (mole dm^{-3}) (NaClO_4)	10^4k_{obs} (s^{-1})	k_2 ($\text{dm}^3\text{mole}^{-1}\text{s}^{-1}$)
10.0	1.0	1.0	8.859	0.089
10.0	1.0	5.0	6.024	0.060
10.0	1.0	10.0	6.579	0.066
10.0	1.0	40.0	6.818	0.068
10.0	1.0	100.0	7.023	0.070
10.0	1.0	150.0	7.143	0.071

However, the reduction of $[(\text{Fe}(\text{saloph}))_2\text{-}\mu\text{-dicarpy}]$ by ascorbic acid showed a decrease in rate of reaction as the dielectric constant decreased from 79.43 - 76.42 ($\text{DMSO}/\text{H}_2\text{O}$) at $[H^+] = 1.0 \times 10^{-4} \text{ mole dm}^{-3}$ (HClO_4), $T = 29.0^\circ\text{C}$, and $I = 1 \times 10^{-3} \text{ mole dm}^{-3}$ (NaClO_4).

This result is indicating that the reaction is occurring between reactants of different charges. The values obtained from varying ionic strength and dielectric constant, D , could be pointing to more than one route for this reaction (Gupta and Gupta, 1981; Iyun *et al.*, 1995; Ukoha, 1999).

Addition of various concentrations of CH_3COO^- , SO_4^{2-} and Cl^- ions gradually increased reaction rate. Anion catalysis has been noted to be characteristic of outer-sphere reaction (Przystas and Sutin, 1973). Also, since ion-pair complex possess no formal charge, interaction with added ions would not be ruled out, thus, suggesting the reaction might have proceeded via ion-pair outer sphere route (Iyun *et al.*, 1995; Ukoha and Iyun, 2002).

The reduction of $\text{Fe}(\text{III})$ complex ion to $\text{Fe}(\text{II})$ as the product was confirmed by reacting the completely reacted mixture with freshly prepared potassium hexacyanoferrate(III) ($\text{K}_3[\text{Fe}(\text{CN})_6]$) gave deep-blue-green colour indicating the presence of $\text{Fe}(\text{II})$.

Gel formation is confirming the participation of free radicals in the reaction as test using acrylamide in excess methanol was positive. It has been documented that mononuclear $\text{Fe}(\text{III})$ species in aqueous solution react with H_2A via free radical intermediates (Kimura *et al.*, 1982). Spectrophotometric data obtained by scanning the reaction mixture as reaction progressed did not show any shift in wavelength of absorption pointing to absence of formation of intermediate complex prior to electron transfer. This does not also rule out its existence, since there may be no build-up of this intermediate.

Effect of temperature

Temperature dependence on the rate of reaction of $[(\text{Fe}(\text{saloph}))_2\text{-}\mu\text{-dicarpy}]$ with L-ascorbic acid was investigated at varying temperature range within $35 - 63^\circ\text{C}$ while other parameters were kept constant. The rate was observed to increase as temperature increased as reported in Table 4.

Table 4: Temperature dependence on rate of reactions of [(Fe(saloph))₂-μ-dicarp] with H₂A at [(Fe(saloph))₂-μ-dicarp] = 1.0 x 10⁻⁵ mole dm⁻³, [H₂A] = 2.0 x 10⁻³ mole dm⁻³, while other parameters were kept constant at λ_{max} = 424 nm

Reductant	Temperature (K)	10 ⁴ k _{obs} (s ⁻¹)	log (k _{obs} /T)	lnk ₂	10 ³ (1/T)(K ⁻¹)
H ₂ A	308	5.417	-5.7547	-1.3063	3.2467
	313	6.086	-5.7112	-1.1897	3.1948
	323	7.015	-5.6631	-1.0478	3.0959
	333	8.148	-5.6113	-0.8979	3.0030
	336	9.091	-5.5677	-0.7885	2.9761

Based on Eyring Equation (5)

$$\log \frac{k_{obs}}{T} = \log \frac{k}{h} + \frac{\Delta S^\ddagger}{2.303R} - \frac{\Delta H^\ddagger}{2.303RT} \quad \dots\dots\dots(5)$$

where k_{obs} = temperature dependent rate constant, k = Boltzmann's constant, h = Planck's constant, ΔS[‡] = entropy of activation, ΔH[‡] = enthalpy of activation and T = temperature. From the plot of log(k_{obs}/T) versus 1/T constructed, activation parameters, ΔH[‡] and ΔS[‡], were determined from slope and intercept. Also, from Arrhenius plot of lnk₂ versus 1/T, activation energy (E_a) was evaluated.

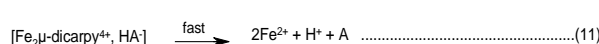
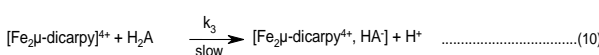
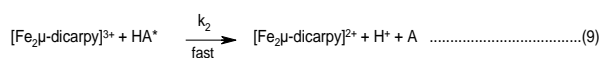
Activation parameters, E_a, ΔH[‡] and ΔS[‡] evaluated from the slope and intercept of Eyring plot gave 14.805 kJmol⁻¹, 12.122 kJmol⁻¹ and -268.86 JK⁻¹mol⁻¹ respectively. Similar results have been reported by other researchers. Ukoha and co-workers (2015) reported the inner sphere path of the reduction of [(Fe(salen))₂adi] by dithionite ion and observed ΔH[‡] = 10.94 kJmol⁻¹ and ΔS[‡] = -291.20 JK⁻¹mol⁻¹. Also, the outer sphere reaction mechanism of the oxidation of L-ascorbic acid by pentaammineaquacobalt(III) ion in aqueous solution had activation parameters; ΔH[‡] = 105 ± 11 kJmol⁻¹ and ΔS[‡] = 93 ± 45 JK⁻¹mol⁻¹ (Dixon *et al.*, 1995).

In this study, the negative entropy value (-268.86 JK⁻¹mol⁻¹) is implicative of well ordered transition state and which indicates formation of ion pair complex of outer sphere character prior to electron transfer. Also, due to high solvation and saturation of the iron(III) dimer, it suggests the dimer is inert to substitution. The relatively high E_a and ΔH[‡] values support the slow rate of reaction (.10⁻⁴ s⁻¹) observed. This is indicative of a reaction requiring high energy to attain transition state.

Michealis-Menten plot of 1/k_{obs} against 1/[H₂A] was linear with positive intercept on the y-axis. This is generally believed to promote inner sphere character.

Reaction mechanism

Based on the observed inverse acid dependence, anion catalysis, free radical participation, and positive intercept of Michealis-Menten plot, a plausible mechanism has been proposed to account for the kinetic data generated for this system.



Equations (8 and 10) are the rate determining step, the rate equation can be written as; $\frac{-d[[Fe_2 - \mu - dicarpy]^{4+}]}{dt}$

$$= K_1 k_1 [Fe_2\mu\text{-dicarpy}^{4+}] [HA] + k_3 [Fe_2\mu\text{-dicarpy}^{4+}] [H_2A] \quad \dots\dots\dots(12)$$

But;

$$HA = K_a \frac{H_2A}{[H^+]} \quad \dots\dots\dots(13)$$

Substituting equation (13) into Equation (12),

$$\frac{-d[[Fe_2 - \mu - dicarpy]^{4+}]}{dt} = K_a K_1 k_1 \frac{[H_2A]}{[H^+]} [Fe_2\mu\text{-dicarpy}^{4+}] + k_3 [H_2A] [Fe_2\mu\text{-dicarpy}^{4+}] \quad \dots\dots(14)$$

Rearranging,

$$\frac{-d[[Fe_2 - \mu - dicarpy]^{4+}]}{dt} = (k_3 + K_a K_1 k_1 [H^+]^{-1}) [Fe_2\mu\text{-dicarpy}^{4+}] [H_2A] \quad \dots\dots\dots(15)$$

Equation (15) agrees with Equation (4) where k₃ = a = 1.2 x 10⁻² dm³mol⁻¹s⁻¹ and K_aK₁k₁ = b = 2.0 x 10⁻⁵ s⁻¹.

Based on the mechanism, the inverse acid dependence is consistent with Equation (6). Positive polymerization test is rationalized by the formation and participation of free radicals in Equation (8).

Conclusion

The kinetics of the reduction of [(Fe(saloph))₂-μ-dicarp] by [H₂A] in perchloric acid medium has been investigated. 1:1 stoichiometry has been established for the reaction. The reaction kinetics exhibits reciprocal dependence on acid, anion catalysis and free radical participation, correspond reasonably well to the rate law and proposed mechanism.

On the strength of these experimental observations, the proposed ion-pair complex formation with outer sphere pathway is plausible.

Acknowledgement

We are grateful to the Department of Biochemistry, Federal University, Wukari, for providing some of the equipment for the research. We also appreciate Amadi C. B., Egwu V. E., Okofu S, and Egah G, for their technical assistance.

References

- Alioke CU, Ukoha PO, Ukwueze NN, Ujam OT & Asegbeloyin JN 2012. Kinetics and Mechanism of the Reduction of N,N'-salicylideneiminoiron(III) Complex Ion by L-ascorbic Acid in Aqueous Acid Medium. *Chem. & Materials Res.*, 2: 48 – 57.
- Ashmawy FM, Ujaimi AR, McAuliffe CA, Parish RV & Pritchard RG 1991. A facile synthesis of [(Fe(salophen))₂O] (salophenH₂ = N,N'-o-phenyleneis(salicylideneimine)) and the X-ray Crystal Structure of [(Fe(salophen))₂O]:DMSO. *Inorg. Chim. Acta.*, 187, 155 – 158.
- Atiga S, Ukoha PO, Ujam TO & Okpareke CO 2013. Kinetics and Mechanism of the Reduction of μ-adi-di{[N,N'-bis(salicylideneethylenediaminoiron(III))] by Dithionate ion. *Transition Met. Chem.*, DOI 10.1007/s
- Atiga, S, Ukoha PO & Ujam OT 2015. Dynamics of Electron Transfer Reaction of Trioxosulfate(IV) Ion with Dinuclear Iron(III)-Salen Complex in Perchloric Acid Medium. *Asian Journal Chem.*, 27(4): 1274 – 1278.
- Birch GG & Parket KJ 1974. Vitamin C- Recent Aspects Physiological and Technological Importance. Applied Science Publisher, London, p. 259.

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- Dixon DA, Sadler NP & Dasgupta TP 1995. Mechanism of the oxidation of L-ascorbic acid by the pentaammineaquacobalt(III) ion in aqueous solution. *Transition Met. Chem.*, 20: 295 – 299.
- Dusek M, Petricek V, Kamenicek J & Sindelar Z 1992. Acta Crystallogr. C, 48, 1579. In Atiga S, Ukoha PO & Ujam OT 2015. Dynamics of electron transfer reaction of trioxosulfate(IV) Ion with Dinuclear Iron(III)-Salen complex in perchloric acid medium. *Asian J. Chem.*, 27(4): 1274 – 1278.
- Gupta SS & Gupta YK 1981. Kinetics and Mechanism of the Iron(III) - Catalysed Oxidation of Hydrazine with Peroxydisulfate in Acid Medium. *Inorganic Chemistry*, 20: 1948.
- Iyun JF, Ayoko GA & Lawal HM 1995. Kinetics and Mechanism of the Reduction of Diaquatetrakis(2,2'-bipyridine)- μ -oxodiruthenium(III) by Ascorbic Acid. *Transition Met. Chem.*, 20: 30 – 33.
- Kennedy BJ, Murray KS, Zwack PR., Horn E, Snow MR & Tiekink ERT 1987. Proc. Indian Acad. Sci. (Chem. Sci.), 98, 99. In: Atiga S, Ukoha PO & Ujam OT 2015. Dynamics of electron transfer reaction of trioxosulfate(IV) ion with Dinuclear iron(III)-Salen complex in perchloric acid medium. *Asian J. Chem.*, 27(4): 1274 – 1278.
- Kimiura M, Yamamoto M & Yanabe S 1982. Kinetics and mechanism of the oxidation of ascorbic acid by Tris(1, 10-phenanthroline)iron(III) complexes in aqueous solution. *J. Chem. Soc. Dalton Trans.*, 423 – 425.
- Kopel P, Sindelar Z & Klicka R 1998. Complexes of Iron(III) Salen and Saloph Schiff Bases with Bridging dicarboxylic and tricarboxylic Acids. *Transition Met. Chem.*, 23: 139 – 142.
- Lawal HM 1997. The Electron Transfer Reactions of Pararosaniline Chloride (Basic Fuchsin) and Trisoxalatocobaltate(III) ion in Acidic Media. Ph D. Thesis, Abubakar Tafawa Balewa University, Bauchi, Nigeria.
- Leal JM, Domingo PL, Garcia B & Ibeas S 1993. Alkali-metal ion catalysis of the oxidation of L-ascorbic acid by hexacyanoferrate(III) in strongly acidic media. *J. Chem. Soc. Faraday Trans.*, 89: 3571 - 3577.
- Liu J, Zhang B, Wu B, Zhang K & Hu S 2007. The Direct Electrochemical Synthesis of Ti(II), Fe(II), Cd(II), Sn(II) and Pb(II) Complexes with N,N'-Bis(salicylidene)-o-phenylenediamine. *Turk. J. Chem.*, 31, 623 – 629.
- Przystas TJ & Sutin N 1973. Kinetic Studies of Anion Assisted Outer sphere Electron Transfer Reactions. *J. Amer. Chem. Soc.*, 95: 5545.
- Prakash A, Gangwar MP & Singh KK 2011. J. Dev. Biol. Tissue Eng., 3: 13; in Atiga S, Ukoha PO & Ujam OT 2015. Dynamics of electron transfer reaction of trioxosulfate(IV) ion with Dinuclear Iron(III)-Salen complex in perchloric acid medium. *Asian J. Chem.*, 27(4): 1274 – 1278.
- Salem IA & Gemeay AH 1996. Kinetics and mechanism of the oxidation of L-ascorbic acid by the N, N'-ethylenebis(salicylideneiminato)manganese(III) complex in aqueous solution. *Transition Met. Chem.*, 21: 130 – 134.
- Soni NR, Sailani R, Khandelwal CL & Sharma PD 2012. Kinetics and mechanism of oxidation of L-ascorbic acid by peroxomonophosphate in aqueous acid medium. wileyonlinelibrary.com
- Ukoha PO 1999. Kinetics and Mechanisms of Redox Reactions of μ -Oxo-bridged Iron(III) Complex Ion, $[\text{Fe}(\text{HEDTA})_2\text{O}]^{2-}$ and Some Oxyanions. Ph D. Thesis. Ahmadu Bello University, Zaria, Nigeria.
- Ukoha PO, Atiga S, Ujam OT, Asegbeyin JN, Okpareke OC & Okereke SOE 2015. Kinetics and Mechanism of Electron Transfer Reaction of an Adipato Bridged Iron(III) – Salen Complex with Dithionite Ion in Perchloric Acid Medium. *Croat. Chem. Acta*, 88(3), 259 – 266
- Ukoha PO & Iyun JF 2002. Oxidation of L-ascorbic acid by $\text{enH}_2[(\text{FeHEDTA})_2\text{O}]\cdot 6\text{H}_2\text{O}$ in Aqueous Media. *J. Chem. Soc. Nig.*, 27: 119.