Electron Transfer Reaction of Semicarbazide and Tetrakis (2, 2'- Bipyridine)-μ-Oxodiiron (III) Complex in Aqueous Acidic Media

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ABSTRACT: The objective of this paper is to evaluate the physicochemical properties of electron transfer reaction of semicarbazide and tetrakis (2, 2'-bipyridine)-μ-oxodiiron (III) complex $[Fe_2O^{4+}]$ in aqueous acidic media at $[H^+] = 0.001$ mol dm^{-3}, $\mu = 0.3$ mol dm^{-3}(NaCl), $T = 27 \pm 0.5$, at $\lambda_{max} = 520$ nm by spectrophotometric method. In the course of the reaction a mole of semicarbazide was consumed by a mole of $[Fe_2O^{4+}]$. The order of reaction is unity dependent on $[Fe_2O^{4+}]$ and zero order dependent on semicabazide and is not H^+ and μ dependent. Addition of cations and anions did not affect the reaction. There was no intermediate formation when a partially reacted reaction mixture and the solution of oxidant were respectively scanned within a wavelength of 400 - 700nm. Absence of spectroscopic evidence of intermediate complex formation suggests that the reaction proceeds by the outer-sphere mechanistic pathway with ion pair character.

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Oxo-bridged diiron compounds are essential parts of metalloenzymes (metalloproteins). The Fe$_2$ units in these enzymes or metalloproteins are bridged by one or two oxygen-based ligands. As these enzymes activate O$_2$ and transfer oxygen atoms to various substrates, the iron centres pass through several oxidation states, though some of these oxidation states may not be stable (Nathan *et al.,* 2005). The involvement of the *μ*-oxo diiron cores of the metalloproteins, hemerythrin, ribonucleotide reductase, and purple acid phosphatase in their biological oxygen-transfer and oxygenation processes is well known (Sheriff *et al.*, 1987). Despite the fact that numerous diiron compounds were previously known, the major focus of the researchers were on their synthesis and characterisation by numerous spectroscopic techniques such as infrared, UV-visibe and nuclear magnetic resonance (Nozaki *et al.,* 1999, Anweting *et al,.* 2017). Studies on the stability of the oxo-diiron in acid aqueous media have been carried out (Ukoha 1999; Ukoha and Iyun, 2001; Idris, 2005; Anweting *et al.,* 2017). Many spectroscopic methods have clearly shown that chemical entity of the type [Fe2(bpy)4O]Cl4, was convincingly a dimer of iron (III) which is oxo-bridged in nature, the compound has a distinct structure with the unit of Fe-O-Fe. The

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magnetic properties of the dimeric species of iron (III) formed can be explained by spin-spin coupling pattern. When these oxo-bridged compounds interacts with protons cleavage of the dimers occurred thereby forming mononuclear specie. This is because the proton reduces the strength of Fe-O-Fe bond, thereby enhancing it cleavage thus forming $[FeL_2(H_2O)_2]^{3+}$ (L= bpy), consequently dimers of iron(III) do not exist in concentrated acid medium. Spectrophotometric technique has been used to study variation in absorbance of dimeric iron(III) complexes which contained 2, 2- bipyridine and 1, 10- phenanthroline as the ligands)David and De Mello, 1973), the phenanthroline compounds showed smaller acid dependence compared to bipyridine compound. The two compounds dissociated in the acid with decolourisation, first order kinetics, and were independent of hydrogen ion concentration when the concentration of acid was very low. Moreover there was no bathochromic or hypsochromic shift in the wavelength of maximum absorption of these compounds, suggesting that there was no formation of intermediate when the dissociation occurred. Similar result have been reported by the earlier researchers (Ukoha, 1999; Ukoha and Iyun, 2001; Idris, 2005; Anweting *et al.,* 2017).

Semicarbazide is an important chemical for synthesis of pharmaceutical products including antimicrobials and related compounds. Its products (semicarbazones and thiosemicarbazones) are known to have an activity of antiviral, antiinfective, and antineoplastic through binding to copper or iron in cells. Proper understanding of the electron transfer reaction between semicarbazide and the diiron complex will complement the much needed kinetic information and will bring to the limelight their electron transfer properties with the aim of explaining and subsequently improving their physico-chemical properties. Consequently, the objective of this paper is to evaluate the physicochemical properties of electron transfer reaction of semicarbazide and tetrakis (2, 2'- bipyridine)-µ-oxodiiron (III) complex in aqueous acidic media.

MATERIALS AND METHODS

Materials and Preparation of Solutions: Tetrakis(2,2'- bipyridine)-µ-oxo-diiron(III) chloride ($[Fe_2(bpy)_4O]Cl_4$) hereafter referred to as Fe_2O^{4+} was prepared, purified and characterised according to the method of (Idris, 2005). A stock solution, 0.5 mol dm^{-3} of semicarbazide hereafter referred as RH_2 (Sigma–Aldrich) was prepared by dissolving 1.393 g of semicarbazide hydrochloride in distilled water in a 25 cm^3 volumetric flask and made up to the mark with distilled water. Stock solutions of 2.0 mol dm^{-3}

(HCl) was made by diluting 8.5 ml of 36% HCl (specific gravity 1.18) in 50 ml standard volumetric flask, then made up to the mark with distilled water. The solution was standardised titrimetrically with standard solution of previously dried Na_2CO_3 using methyl red as indicator (Chimere *et al.,* 1985). Stock solutions of sodium chloride, sodium nitrate, sodium formate, potassium chloride and magnesium chloride were prepared from analar grade salts and their various concentrations were obtained by serial dilution.

Stoichiometry: The stoichiometry of the reactions was determined by spectrophotometric titration at $\lambda_{max} = 520$ nm using the mole ratio technique (Ukoha and Iyun, 2001, 2002; Anweting *et al.,* 2023). The concentration of Fe_2O^{4+} was kept constant at 5.0×10^{-5} mol dm^{-3} while that of RH_2 was varied between $(1.0 – 12.0) \times 10^{-5}$ mol dm^{-3} at $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} and constant ionic strength of 0.3 mol dm^{-3}(NaCl) at T = 27 ± 0.5°C. The reactions were allowed to stand until the repeated absorbances of the reaction mixture at $\lambda_{max} = 520$nm were constant. The stoichiometry was then determined from the plots of absorbance versus mole ratio of $Fe_2O^{4+} : RH_2$

Kinetic Studies: The rate of reaction was studied under pseudo-first order condition with $[RH_2]$ in at least 40 folds excess over $[Fe_2O^{4+}]$ at the stated conditions by monitoring the increase in the absorbance of the complex at 520 nm using Corning Colorimeter 252. From the slopes of pseudo-first order plots of log $(A_\infty - A_t)$ versus time, the pseudo-first order rate constant (k_1) were determined (Idris *et al.,* 2007; Anweting *et al.,* 2012a , b; Johnson *et al.,* 2023 Myek *et al.,* 2024).

Acid Dependence Studies: The effect of changes in the hydrogen ion concentration, $[H^+]$ on the reaction rate was investigated by keeping the concentration of the other reactants constant while varying the hydrogen ion concentration in the range $(4 – 14) \times 10^{-4}$ mol dm^{-3} (Adetoro *et al.,* 2010, 2021; Anweting *et al.,* 2012c , d; Jones *et al.,* 2023a, b).

Effect of Ionic Strength (I): The effect of ionic strength on the rates of the reaction was studied over a range of $(1.0 - 6.0) \times 10^{-1}$mol dm^{-3} using NaCl, while others reaction conditions were kept constant (Osunlaja, *et al.,* 2012; Osunlaja, 2014; Adetoro *et al.,* 2024).

Influence of Added Anions and Cations: The influence of added nitrate, formate, potassium and magnesium ions on the rate of reaction were investigated by varying the concentration of these

anions while keeping $[Fe_2O^{4+}]$, $[RH_2]$ and ionic strength constant.

Test for Participation of Free Radicals in the Course of Reaction: Test for free radicals was carried out by adding 2 g of acrylamide to a partially oxidised reaction mixture containing various concentrations of oxidant, reductant and hydrogen ion. A large excess of methanol was added to the reaction mixture. Control experiment was carried out by adding acrylamide to solutions of oxidant and reductant separately at the same conditions of $[H^+]$, and temperature. Any polymerisation as indicated by gel formation suggested the presence of free radicals in the reaction mixture (Hamza *et al.,* 2012; Babatunde and Ajayi, 2013).

Analysis of Products: When the reaction was completed, the reaction mixtures were probed in order to know possilbe organic and inorganic products formed in the course of the reaction. Fourier Transform Infrared (FTIR) was used for this purpose.

RESULTS AND DISCUSSION

Colorimetric titration by the used of mole ratio technique depicted that one mole of Fe_2O^{4+} was consumed by one mole of semicarbazide in the course of the reaction. The stoichiometry of 1:1 $(Fe_2O^{4+} : RH_2)$ obtained in the reaction is represented in equation 1 as:

$$Fe_2O^{4+} + RH_2 \longrightarrow 2Fe^{2+} + R + H_2O \quad (1)$$
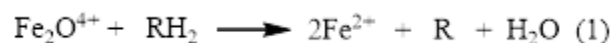
The stoichiometric coefficient of 1:1 deduced from this research is similar to the results of other authors for the oxidation of catechol , thiourea and glutathione (Idris *et al*., 2004, Anweting *et al.,* 2017, 2021) by $Fe_2(bipy)_4O^{4+}$ and for the oxidation of ascorbic acid by $[(FeHEDTA)_2O]^{2-}$(Ukoha, 1999).

The reaction was unity order in $[Fe_2O^{4+}]$ on the ground that, the graph of log $(A_\infty - A_t)$ versus time using the relation:

$$\log(A_\infty - A_t) = \frac{k_1 t}{2.303} + \log(A_t - A_\infty) \quad (2)$$

was linear for about 70% of the reaction time (Figure 1).

From the slope of the graph, k_1 was deduced whereas the order in $[RH_2]$ was zeroth order due to the fact that there was no change in the value of k_1 within the range of the concentrations of RH_2 studied. Similarly, using the Van't Hoff differential equation (Onu, 2010).

$$R = k[A]^n \quad (3)$$

Where $[A]$ is the concentration of the substrate. The values of the slopes were zero for the reductant. The organic components of the reaction involving the reductant and the oxidant in this study was tested for by the used of Fourier Transform Infrared spectroscopy technique. Figures 2 and 3 respectively show the spectra of the reductant and the products of the reactions. From Figure 2, the spectrum of the reductant, the vibrational frequencies at 3252.09cm^{-1} and 3430.51cm^{-1} are due to symmetrical and asymmetrical stretching of NH_2 respectively (Janarthanan *et al.,* 2011; Binil *et al.,* 2012). The vibrational frequency at 1687.77cm^{-1}, comes from ν(C=O) stretching of the molecule. From Figure 3, which is the FTIR spectrum of the product, it is highly apparent that the carbonyl functional group present in the semicarbazide (reductant) is still conspicuous in the product, the vibrational frequency of 1644.37cm^{-1} is from carbonyl functional group. Based on the FTIR spectroscopy for the determination of the organic product of the reaction, it is apparently conspicuous that the C=O functional group seen in the reductant is also present in the product. Moreover, it can be inferred that the spectrum of semicarbazide differs from that of the product by the numbers of hydrogen present in each of the spectra. Consequently, from the two spectra (Figures 2 and 3) the number of hydrogen in the spectrum of semicarbazide is more than that of the product. Which therefore implies that dinuclear complex of iron (III) was reduce by semicarbazide in the course of the reaction.
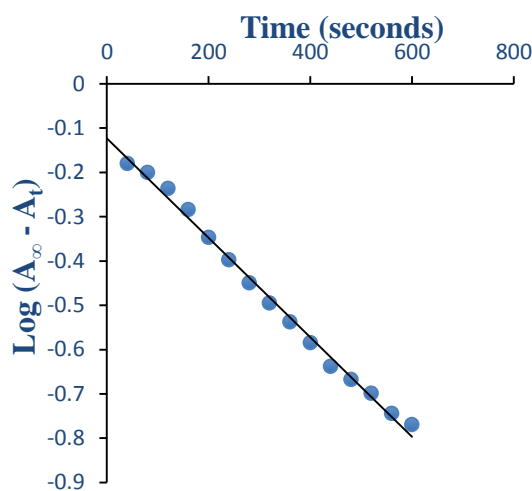
Fig. 1: Typical pseudo-first order plot for the redox reaction of Fe_2O^{4+} with RH_2 at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[RH_2] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 27.0 ± 0.5^{o}C and λ_{max} = 520 nm
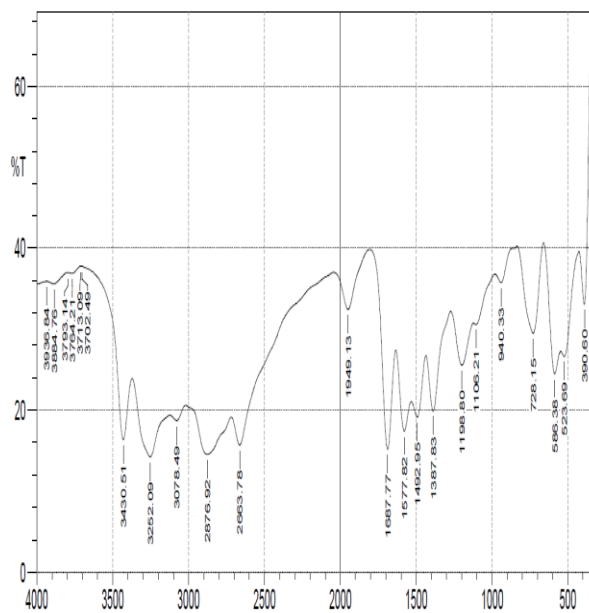
Fig 2: FTIR spectrum of RH$_2$
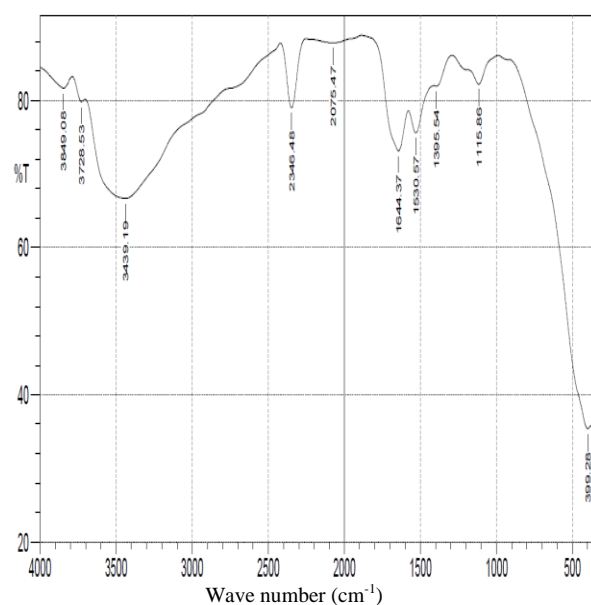
Fig 3: FTIR spectrum of the product of reaction of Fe$_2$O^{4+} and RH$_2$

The rate of reaction between Fe$_2$O^{4+} and RH$_2$ was relatively unaltered within the range of acid concentration (4.0 - 14.0) $\times$ 10^{-4} mol dm^{-3} used for this studies, in a nutshell addition of proton did not affect the rate of reaction (Table 1). Despite the fact that the effect of hydrogen ion on the reaction that involved semicarbazide and any given oxidising agent have not been reported previously. From the scheme of the reaction the expectation would have been the deprotonation of two moles of protons from semicarbazide in the reaction mixture prior to the combination with the oxidant. The deprotonated

molecules of protons thereafter combined with oxo-anion from the cleavaged of binuclear complex of iron(III) to produce water as shown in Equation 1. The rate of reaction remain unaltered when anions were added to the reaction that involved semicarbazide and binuclear complex of iron(III). Free radicals were not formed during the reaction because there was no gel formation when acrylamide was added to the reaction mixture followed by excess methanol.

Table 1: Pseudo-first order rate constants for the redox reaction of Fe$_2$O^4 – RH$_2$ in aqueous HCl medium, λ_{max} = 520nm, I = 0.30 mol dm^{-3} (NaCl), [Fe$_2$O^{4+}] = 2 $\times$ 10^{-4} mol dm^{-3}, T = 27.0 ±0.5°C

10^4[RH$_2$] (mol dm^{-3})	10^3 [H$^+$] (mol dm^{-3})	10^2 [I] (mol dm^{-3})	10^4 k$_1$ (s^{-1})
40.0	10.0	30.0	15.1
60.0	10.0	30.0	15.7
80.0	10.0	30.0	15.8
100.0	10.0	30.0	15.8
120.0	10.0	30.0	16.0
140.0	10.0	30.0	16.0
160.0	10.0	30.0	16.0
60.0	4.0	30.0	14.1
60.0	6.0	30.0	13.4
60.0	8.0	30.0	13.4
60.0	10.0	30.0	13.8
60.0	12.0	30.0	12.1
60.0	14.0	30.0	13.0
60.0	10.0	10.0	15.6
60.0	10.0	20.0	15.6
60.0	10.0	30.0	15.6
60.0	10.0	40.0	15.0
60.0	10.0	50.0	15.3
60.0	10.0	60.0	15.3

Alteration in the concentration of inert electrolyte (ionic strength) did not alter the rate of the reaction. Lack of the alteration of the rate of reaction as ionic strength increases is due to no charge on one or both of the reacting species. Moreover, lack of the dependence of the rate of reaction on the ionic strength can also be due to the presence of ion-pair complex. This is because the ion-pair complex does not possess a formal charge, it has been reported (Iyun *et al*., 1992, 1995; Anweting *et al.,* 2021; Johnson *et al.,* 2023) that the rate of reaction with outersphere character which involved ion pair is independence of variations in ionic strength.

Lack of dependence of the reaction rate on ions addition is in accordance with the formation of ion – pairs in the reaction before the electron transfer. Interaction or reaction between the added ions and the ion-pair would not be possible because the ion-pair complex does not possess formal charge thus depicting that the reaction can be rationalized by outerspere mechanistic scheme. Reactions that involved ion-pair complex through outerspere pathways have been reported by several authors (Iyun

et al., 1995; Ukoha, 1999; Idris, 2005; Anweting *et al.,* 2017, 2021; Johnson *et al.,* 2023).

There was no bathochromic or hypsochromic sbift from the wavelength of maximum absorption at 520 nm when the reaction mixture was scanned in spectrophotometer. Thus suggesting the absence of spectroscopic detectable intermediates in the course of the reaction. On the basis of the above results, the reaction occurred through the outersphere pathway and the mechanism has been proposed as follows:

$$RH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RH^{\cdot} + H^+$$

$$Fe_2O^{4+} + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe_2OH^{5+}$$

$$Fe_2OH^{5+} + RH^{\cdot} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe_2OH^{5+}, R^{2-}] + H$$

$$[Fe_2OH^{5+}, R^{2-}] \overset{k_4}{\underset{slow}{\longrightarrow}} Fe_2OH^{4+} +]$$

$$Fe_2OH^{4+} + R^{\cdot} \overset{k_5}{\longrightarrow} Fe_2OH^{3+} +]$$

$$Fe_2OH^{3+} + H^+ \overset{k_6}{\longrightarrow} 2Fe^{2+} + H_2O$$

$$Rate = k_4[Fe_2OH^{5+}, R^{2-}] \quad (10)$$
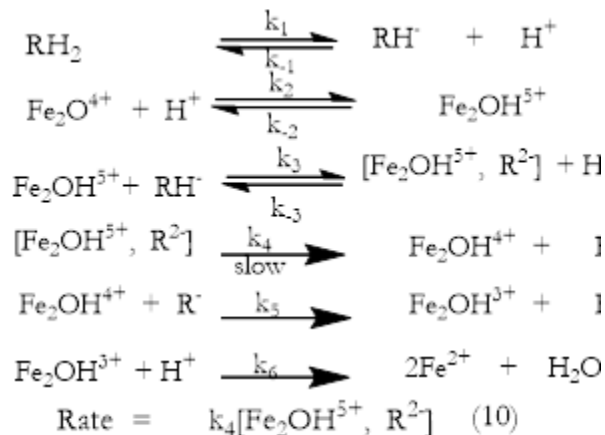
Application of steady state hypothesis for $[Fe_2OH^{5+}, R^{2-}]$ gives:

$$k_3[Fe_2OH^{5+}][RH^{\cdot}] - k_{-3}[Fe_2OH^{5+}, R^{2-}][H^+] - k_4[Fe_2OH^{5+}, R^{2-}] = 0 \quad (11)$$

$$[Fe_2OH^{5+}, R^{2-}] = \frac{k_3[Fe_2OH^{5+}][RH^-]}{k_{-3}[H^+] + k_4} \quad (12)$$

Application of steady state hypothesis for $[Fe_2OH^{5+}]$ gives:

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2O^{4+}][H^+]}{k_{-2} + k_3[RH^-]} \quad (13)$$

If $k_{-3}[H^+] \gg k_4$ equation 12 reduces to

$$[Fe_2OH^{5+}, R^{2-}] = \frac{k_3[Fe_2OH^{5+}][RH^-]}{k_{-3}[H^+]} \quad (14)$$

From equation 13, if $k_{-2} \ll k_3[RH^-]$ then the equation reduces to

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2O^{4+}][H^+]}{k_3[RH^-]} \quad (15)$$

Substituting equation 15 into 14 gives:

$$[Fe_2OH^{5+}, R^{2-}] = \frac{k_2 k_3[Fe_2O^{4+}][H^+][RH^-]}{k_{-3}[H^+]k_3[RH^-]} \quad (16)$$

$$[Fe_2OH^{5+}, R^{2-}] = \frac{k_2}{k_{-3}}[Fe_2O^{4+}] \quad (17)$$

Substituting equation 17 into 10 gives :

$$Rate = \frac{k_2}{k_{-3}}[Fe_2O^{4+}] \quad (18)$$

Where $\frac{k_2}{k_{-3}} = k_{obs}$ (19)

$$\therefore Rate = k_{obs}[Fe_2O^{4+}] \quad (20)$$

The proposed mechanism for the reactions involve multiple elementary steps, which is the summation of what happened from the beginning of the reaction to the formation of products. From the mechanism of the reaction one mole of Fe_2O^{4+} reacted with a mole of RH_2 which is in consonant with equation 1. The rate determining step (slow step) is represented by equation 7, the overall rate equation (equation 20) depicts that the reaction is zero order dependent on RH_2, owing to the fact the value of k_1 was constant throughout when the concentrations of RH_2 were varied. Similar mechanisms have been proposed (Idris, 2005; Anweting *et al.,* 2017, 2021; Johnson *et al.,* 2023). The mechanism was rationalised in favour of outersphere pathway.

Conclusion: The empirical kinetic data from this research showed that the reaction is unity order in oxidant and zero order in reductant, and that variation in the concentration of hydrogen ion, ionic strength and addition of ions did not have any effect in the reaction. The reaction displayed negative result for free radical test, formation of intermediate complex could not be detected spectroscopically prior to the electron transfer when the reaction mixture was scanned, the mechanism of the reaction was proposed to be in favour of outersphere mechanism with ion pair property.

Competing interests: The authors declare that they have no known competing financial interests

Data Availability Statement: Data are available upon request from the first author or corresponding author.

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