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Electron Transfer Reactions of Tetrakis (2, 2- Bipyridine)-μ Oxodiiron(III) Complex and Dithionate Ion in Aqueous Acidic Media: Kinetic and Mechanistic Approach

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Abstract: *Electron transfer reaction of tetrakis(2,2'- bipyridine)-μ-oxodiiron(III) complex (Fe_2O^{4+}) and dithionate ($S_2O_6^{2-}$) has been carried out in aqueous hydrochloric acid. The reaction was carried out at $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = .3.0 × 10^{-1} mol dm^{-3}(NaCl), T= 26 ± 1°C, and λ_{max} = 520nm. The stoichiometric ratio of the reaction is 1:1.The reaction is first order with respect to $[Fe_2O^{4+}]$ and zero-order on $[S_2O_6^{2-}]$ and is not hydrogen ion and ionic strength dependent. Added anions and cations do not affect the reaction, there was no gel formation upon the addition of acrylamide and excess methanol to the reaction mixture, which shows the absence of polymerisation, The products of the reaction were identified as Fe^{2+} and SO_4^{2-}. With recourse to empirical data, the reaction is rationalised to occur via an outer sphere pathway with ion pair character. A Plausible mechanism has been proposed for the reaction.*

Keywords: *Electron transfer, kinetics, mechanism, dithionate*

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1.0 Introduction

The process of electron transfer (ET) is of immense benefit in the development of science and technology since many reactions in physical, chemical, biological and bioinorganic systems involve the transfer of electrons at one stage or another (Bixon and Jortner, 1997; Barbara *et al.*, 1996; Anweting *et al.*, 2018). In nature, ET occurs in a photosynthetic reaction centre where the transfer of electrons is used to create charge imbalance across a membrane, originating a proton pumping mechanism to produce adenosine triphosphate (ATP). In oxidative phosphorylation, nicotinamide adenine dinucleotide reduced form (NADH) releases electrons to dioxygen, to form water and a substantial amount of excess energy, used for the production of ATP. In a chemical system, ET at the metal surface with oxygen is responsible for corrosion. Solid-state electronics depend on the control of the ET in semiconductors and the new area of molecular electronics depends critically on the understanding and the control of the transfer of electrons in and between molecules (Marcus and Siddarth, 1992).

Chemical kinetics attempts to answer the question of what happens as reactants are converted to products. Does the reaction occur in one step, or multiple steps via intermediates? The rates of chemical reactions are of great importance in industrial and biological processes, especially in determining optimum reactions as in organic synthesis and chemical manufacturing

(Chigwada-Razunguzwa, 2005). Many rate constants have now been measured and they have stimulated a variety of theoretical studies. Kinetics has been characterised by a strong interplay of theory and experiment, which now includes the testing of theoretically predicted quantitative correlations.

Scientists use kinetic studies to postulate theories to replicate natural occurrences, calculate how fast the products of reactions could be formed and use thermodynamics to predict the equilibrium composition of the reaction mixtures. The economic viability of many industrial processes is largely affected by the rate at which the reactions can occur. Also, every chemical reaction taking place in living organisms occurs at a rate carefully controlled by the biological catalysts called enzymes. Life would have been impossible without the rates of countless, complicated chemical processes being controlled with exceptional precision by exquisitely formed enzymes (Muhammad, 2003).

Moreover, the technique chosen for monitoring the rate of reaction depends on whether the reaction is slow or fast. Conventional techniques are used for slow reactions. Nevertheless, this technique is difficult for fast reactions because the time require to bring the reactants to a particular temperature or measure a concentration may be quite significant when compared to the half-life of the reaction. Thus, special techniques are employed in the rapid transfer and mixing of substrates.

The chemistry of binuclear complexes of iron has continued to be of great interest in the past decades because of the presence of such di-iron centres in a variety of non-haem iron proteins. Involvement of the μ-oxo di-iron cores of the metals-proteins, hemerythrin, ribonucleotide reductase, and purple acid phosphatase in their biological oxygen-transfer and oxygenation processes is well known, (Ukoha, 1999; Anweting, 2016). Though the binuclear complexes of iron have been known for a long time, to a large extent, greater attention was on their synthesis and characterisation. Several di-iron(III) complexes have been prepared and characterised using numerous spectroscopic techniques such as infrared, UV-visible and nuclear magnetic resonance (Nozaki *et al.*, 1999). The stability of the di-iron in aqueous and acid media has been studied (Ukoha and Iyun, 2001; Idris, 2005; Anweting, *et al*., 2017; Anweting, *et al*., 2021). Dithionates are oxyanions of sulphur which are good reducing agents. The reducing property of the dithionate ions has made it gain wide application in photographic processing as a fixer and is also used in gold extraction. However, we deemed it necessary to carry out this study due to the paucity of kinetic data of the electron transfer reaction between the binuclear complex of iron and dithionate ion, which is a reducing agent. We therefore envisage that the data that would be generated from this research will be useful for chemists.

2.0 Materials and Methods

2.1 Materials

Chemical reagents used in this research were of analytical grade, distilled water was used throughout for all solutions preparation. The synthesis and characterisation of tetrakis(2,2'-bipyridine)-µ-oxo-di-iron(III) chloride was carried out as explained elsewhere (Idris, 2005) and (Anweting, 2016). The complex was not stabled in $[H^+] > 2.0 \times 10^{-2}$ mol dm^{-3} hence, kinetics were carried out within $(3.0 \leq [H^+] \leq 14.0) \times 10^{-3}$ mol dm^{-3}. The solution of Fe_2O^{4+} was always freshly prepared when needed and covered with foil paper before stoichiometric and kinetic investigations. A stock solution of HCl was made by diluting analar grade hydrochloric acid (36%, specific gravity 1.18) and standardised using a standard solution of previously dried Na_2CO_3.

2.2 Stoichiometric coefficient of the reaction

The quantitative relationship between the two reactants was determined by spectrophotometric titration by the use of the mole ratio method (Ukoha and Ibrahim, 2004; Anweting *et al*,. 2012a, b, c and d). The concentration of the binuclear complex of iron(III) was kept constant while that of the reductant (dithionate) was varied between the mole ratio 1:0.5 to 1:3.

The reactions were allowed to go to completion and the absorbances of the completely reacted mixtures (A_∞) were monitored at 520 nm (λ_{max} of Fe_2O^{4+}) using Corning Colorimeter 253. The absorbances obtained were plotted against the mole ratios of the reactant. Points of inflexion in these plots gave the stoichiometry of the reactions.

2.3 Kinetic measurements

The rates of reactions of the Fe_2O^{4+} with the reductant were studied by monitoring the increase in absorbance of the binuclear complex of iron(III) at λ_{max} (520 nm) spectrophotometrically. All kinetic measurements were carried out under pseudo–first order conditions with reductant concentrations in excess of the oxidant concentrations at fixed temperature, ionic strength and [H^+] (Onu and Iyun, 2000; Osunlaja, 2014; Jones *et al.,* 2023a and b). The pseudofirst–order plots of log (A_∞-A_t) against time were made and the slopes of the plots gave the pseudofirst–order rate constants, k_{obs}.

The effect of changes in the hydrogen ion concentration, H^+ on the reaction rate was investigated by keeping the concentrations of the oxidant and the reductant constant while that of the hydrogen ion concentration was varied. Ionic strength, I, was maintained constant at the stated temperature at 3.0×10^{-1} mol dm^{-3} [NaCl] (Ukoha *et al.*, 2010).

The primary salt effect (ionic strength) on the rate of reaction was investigated by varying the ionic strength, I of the reaction mixture between $(1.0 – 6.0) \times 10^{-1}$ mol dm^{-3} [NaCl] while maintaining the concentrations of the oxidant, reductant and hydrogen ion constant at stated reaction temperature (Ukoha *et al.,* 2015).

2.4 Effect of changes in dielectric constant (D) of the reaction medium on rate

The effect of change in the dielectric constant of the reaction medium on the reaction rate was investigated by adding various amounts of acetone to the reaction mixture. The concentrations of the oxidant, reductant and hydrogen ion as well as the ionic strength were maintained constant (Idris, 2005; Anweting, 2016).

2.5 Ions catalysis

The effect of added ions on the reaction rate was observed by the addition of various amounts of ions (Mg^+, K^+, NO_3^-, and $HCOO^-$) while maintaining the oxidant, reductant and hydrogen ion concentrations constant. The ionic strength and temperature were maintained constant, also (Ukoha and Ibrahim, 2004; Anweting *et al.*, 2023).

2.6 Test for the 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 for the reaction system. A large excess of methanol was added to the reaction mixture. The control experiment was carried out by adding acrylamide to solutions of oxidant and reductant separately at the same conditions of [H^+], I and temperature. Any polymerisation as indicated by gel formation suggested the presence of free radicals in the reaction mixture.

2.7 Test for the formation of the intermediate complex before electron transfer

Test for the presence of stable, detectable intermediate complexes formed in the course of the reaction was carried out by recording the electronic spectra of partially reacted reaction mixtures at various time intervals depending on the speed of the reaction. Similar runs were made for reactants separately in each case. A shift in or consistent, λ_{max} and/ or enhancement of peak as the reaction progressed is determined (Mohammed *et al.*, 2014a and b).

2.8 Product analysis

After the completion of the reaction, the reaction mixtures were analysed for the type of products formed at the end of the reaction. The products were confirmed by chemical tests and spectroscopic methods.

3.0 Results and Discussion

Determination of stoichiometry using spectrophotometric titration depicted that one mole of $S_2O_6^{2-}$ is oxidised per mole of Fe_2O^{4+} and is shown in equations 1.

$$Fe_2O^{4+} + S_2O_6^{2-} + H_2O \rightarrow 2Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

Similar stoichiometry was also reported in the reaction of dithionate with toluidine blue (Babatunde and Ajaiyi, 2013), nonetheless, in the reaction between $[FeSalen(H_2O)_2]^+$ and dithionate, two moles of the oxidant were consumed by one mole of dithionate (Ukoha *et al.*, 2010). Kinetic studies of the reduction of Fe_2O^{4+} by and $S_2O_6^{2-}$ indicated a first-order model which showed a strong dependence on the [oxidant]. Pseudo-first-order plots of log (A_∞ - A_t) versus time were linear (Fig. 1) for about 75% of the extent of the reaction concerning reductant. The values of k_{obs} evaluated from the slopes of the pseudo-first-order plots were relatively constant within the range of the concentrations of reductant studied. Hence the alteration in the concentration of the reductant does not affect the rate of the reaction and the reaction was zero order dependence on $[S_2O_6^{2-}]$ as shown in equation 2 and Table 1

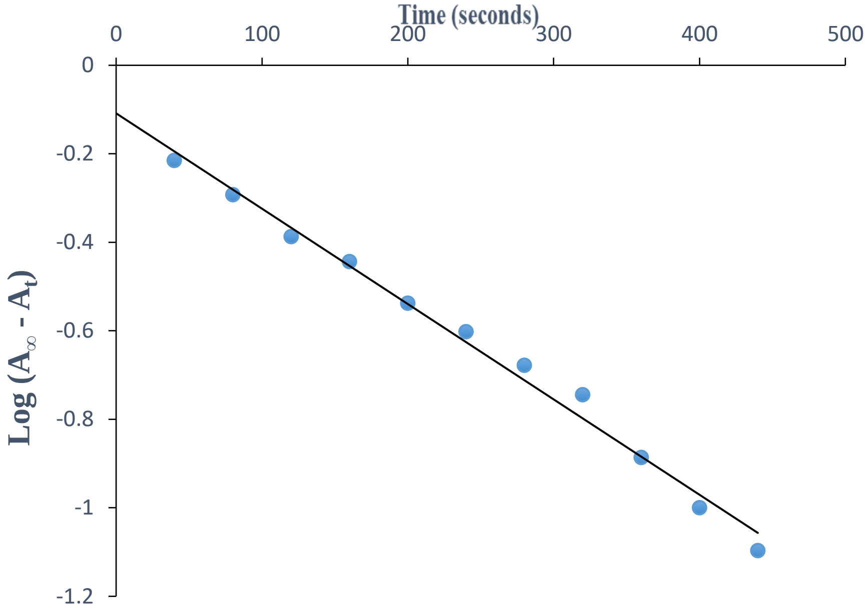

Fig. 1: Typical Pseudo-first order plot for the electron reaction of $Fe_2O^{4+}$and $S_2O_6^{2-}$ at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[S_2O_6^{2-}] = 14.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 26.0 ± 1.0°C and λ_{max} = 520 nm

$$\frac{d}{dt}[Fe_2O^{4+}] = k_{obs}[Fe_2O^{4+}] \qquad (2)$$

The zero-order dependence on the reductant is analogous to the report given by Idris (2005), in the reaction between Fe_2O^{4+} and sulphur oxyanions ($S_2O_3^{2-}$ and $S_2O_5^{2-}$). Nevertheless, a first-order dependence on oxidant and reductant were reported in the reaction of dithionite with monomethyl fuchsin (Onu & Iyun, 2000), toluidine blue (Hamza *et al.*, 2012), malachite green (Idris *et al.*, 2015) and Ru_2O^{4+} (Mohammed, 2015).

Within the acid range of $(4.0 - 14) \times 10^{-4}$ mol dm^{-3}, the rate of reaction was independent of $[H^+]$ in the reaction of Fe_2O^{4+} with the reductant. Non-dependence nature of acid on the rate of the reactions has been reported by Idris (2005) in the reactions of Fe_2O^{4+} with $S_2O_3^{2-}$, $S_2O_5^{2-}$, mercaptoacetic acid, L-cysteine, 1,2-benzendiol and 1,3-benzenediol.

Table 1: Pseudo-first order rate constants for the electron transfer reaction of e_2O^{4+} and $S_2O_6^{2-}$ in aqueous HCl medium, λ_{max} = 520 nm, I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}]$= 2 × 10^{-4} mol dm^{-3} , T = 26.0 ±1.0 °C

$10^3[S_2O_6^{2-}]$ (mol dm^{-3})	10^2 $[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^3 k_{obs} (s^{-1})
2.0	1.0	3.0	1.88
4.0	1.0	3.0	1.88
6.0	1.0	3.0	1.92
8.0	1.0	3.0	2.01
12.0	1.0	3.0	2.06
14.0	1.0	3.0	2.06
6.0	1.0	3.0	2.02
6.0	0.4	3.0	1.90
6.0	0.6	3.0	1.81
6.0	0.8	3.0	1.85
6.0	1.0	3.0	1.90
6.0	1.2	3.0	1.89
6.0	1.4	3.0	1.91
6.0	1.0	1.0	1.97
6.0	1.0	2.0	2.01
6.0	1.0	3.0	1.91
6.0	1.0	4.0	1.97
6.0	1.0	5.0	1.94
6.0	1.0	6.0	1.87

It was also observed that at greater than 2.0 × 10^{-3} mol dm^{-3} of $[H^+]$, Fe-O-Fe was unstable and cleavage of the oxo-bridge resulted in a change of colour of the complex from brown to deep red.

The unstable nature of the oxo-bridge (Fe-O-Fe) in acid solutions was reported by earlier researchers, (Idris, 2005; Anweting, 2016). The presence of acid weakens Fe-O-Fe bond due to protonation at the bridged oxygen, thereby forming mononuclear species and the process is supposed to result in direct acid dependence. Notwithstanding, the non-dependence of the rate of change in $[H^+]$ in the reaction suggests that the protonation was very fast and the equilibrium constant for the protonation was infinitesimal.

There was no significant change in the rate of reaction when the ionic strength of the reaction media was varied between (1.0 – 6.0) × 10^{-1} mol dm^{-3} (NaCl), as shown in Table 1. Non-dependence of the rate of reaction on ionic strength is a common characteristic of reaction occurring between ion and neutral species, where the products of charges are zero at the transition state (Atkins, 1979) and could also be due to ion-pair interaction at the activated complex. Since the ion-pair complex does not possess a formal charge, the rate of reaction would not be affected by changes in ionic strength if ion-pairs are involved in reactions with outer-sphere character.

By using a water-acetone mixture at various proportions, the dielectric constant of the reaction medium varied between 81 – 68.27. The studies showed that changes in D did not affect the reaction rates (Table 2). This suggests that the reaction occurred between a cation and a neutral molecule or free radical. This is also consistent with a reaction involving ion pairs with outer sphere character.

Table 2 : Dependence of rate of reaction on dielectric constant of $[Fe_2O^{4+}]$- $[S_2O_6^{2-}]$ system at I = 0.3 mol dm^{-3} , (NaCl), $[S_2O_6^{2-}]$ = 6.0 × 10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3}, λ_{max}=520nm, $[H^+]$ = 1.0 × 10^{-3}mol dm^{-3}, T = 26.0 ± 1.0 °C

D	10^3 k_{ads} (s^{-1})
81.00	1.95
79.31	1.89
75.54	1.89
73.73	1.91
70.09	1.91
70.09	1.91
68.27	1.91

The addition of anions and cations did not have any effect on the rate of reaction as shown in Table 3.

The absence of ion catalysis indicates that the formation of ion pairs in the reaction is preceded by electron transfer. Since the ion-pair complex does not have a formal charge, interaction with added ions will not be possible suggesting that the reaction might have proceeded by the outersphere pathway.

The non-dependence of the added ions on the rate, however, further depicts that the reactant ions are not connected at the activated complex. Formation of ion-pair intermediates have been reported in the reaction of Ru_2O^{4+} with 2-mercaptoethanol, 2-mercaptoethylamine (Iyun *et al.*,1995) and thioureas (TU, ATU, MTU and DMTU) (Mohammed *et al.*, 2014a, b; Mohammed, 2015), $[(FeHEDTA)_2O]^{2-}$ with mercaptoacetic acid (Ukoha, 1999) and Fe_2O^{4+} with $S_2O_3^{2-}$, $S_2O_5^{2-}$, mercaptoacetic acid, L-cysteine, 1,2-benzenediol and 1,3-benzenediol (Idris, 2005). There was no stable intermediate complexes formation when spectroscopic studies were carried out because there was no shift in λ_{max} , but an isosbestic point was obtained at 520nm. The SO_4^{2-} was identified qualitatively by the formation of white precipitate on the addition of HCl and $BaCl_2$ solution to the product of the reaction.

The plausible reaction pathway that is consistent with the above kinetic data is proposed as:

$$Fe_2O^{4+} + S_2O_6^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe_2O^{4+}, S_2O_6^{2-}] \qquad (3)$$

$$[Fe_2O^{4+}, S_2O_6^{2-}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe_2O^{3+} + S_2O_6^{-} \qquad (4)$$

$$Fe_2O^{3+} \xrightarrow[\text{slow}]{k_3} Fe^{2+} + FeO^{+} \qquad (5)$$

$$FeO^{+} + S_2O_6^{-} \xrightarrow{k_4} Fe^{2+} + S_2O_7^{2-} \qquad (6)$$

$$\text{Rate} = k_3[Fe_2O^{3+}] \qquad (7)$$

Application of steady state hypothesis for $[Fe_2O^{3+}]$ gives:

$$[Fe_2O^{3+}] = \frac{k_2[Fe_2O^{4+},\ S_2O_6^{2-}\ ]}{k_{-2}[S_2O_4^{-}] + k_3} \qquad (8)$$

Substituting equation (8) into (7) gives

$$\text{Rate} = \frac{k_3k_2[Fe_2O^{4+},\ S_2O_6^{2-}\ ]}{k_{-2}[S_2O_6^{-}] + k_3} \qquad (9)$$

If $k_3 \ll k_{-2}[S_2O_6^{-}]$Equation (9) gives

$$\text{Rate} = \frac{k_3k_2[Fe_2O^{4+},\ S_2O_6^{2-}\ ]}{k_{-2}[S_2O_6^{-}]} \qquad (10)$$

From equation 3

$$[Fe_2O^{4+},S_2O_6^{2-}] = \frac{k_1}{k_{-1}}[Fe_2O^{4+}][S_2O_6^{2-}] \qquad (11)$$

Substituting equation 11 into 10 gives:

$$\text{Rate} = \frac{k_1k_2k_3}{k_{-1}}\frac{[Fe_2O^{4+}][S_2O_6^{2-}]}{k_{-2}[S_2O_6^{-}]} \qquad (12)$$

If $[S_2O_6^{2-}] \approx k_{-2}[S_2O_6^{-}]$ equation 12 reduces to:

$$\text{Rate} = \frac{k_1k_2k_3}{k_{-1}}[Fe_2O^{4+}] \qquad (13)$$

$$\text{Where } \frac{k_1k_2k_3}{k_{-1}} = k_{obs} \qquad (14)$$

$$\therefore \text{ rate} = k_{obs}[Fe_2O^{4+}] \qquad (15)$$

Thus equation 15 is similar to equation 2.

Table 3: Dependence of rate constant on added anions and cations for the electron transfer reaction of [Fe_2O^{4+}] and $S_2O_6^{2-}$]

10^3 [NO_3^-] (mol dm^{-3})	10^2 k_{obs} (s^{-1})
20.0	1.88
60.0	1.97
100.0	1.92
120.0	1.93
10^3 [$HCOO^-$] (mol dm^{-3})	
20.0	1.97
60.0	1.93
100.0	1.93
120.0	1.90
10^3[K^+](mol dm^{-3})	
20.0	1.91
60.0	1.88
100.0	1.93
120.0	1.95
10^3 [Mg^{2+}] (mol dm^{-3})	
20.0	1.88
60.0	1.93
100.0	1.93
120.0	1.93

4.0 Conclusion

Based on the proposed plausible mechanistic pathway, since Fe_2O^{4+} is coordinatively saturated, there would be substitution inertness thereby the ease of a ligand–bridged intermediate of inner-sphere character is completely ruled out. Thus, the reaction followed the outer sphere with an ion-pair character. This substantiation is further supported by (a) The negative result of the polymerisation test suggests the absence of free radical intermediate in the reaction or the equilibrium constant for the formation of such radicals can be assumed to be negligible (Idris, 2005). (b) The absence of spectrophotometric evidence for precursor complex as scanning the reaction mixture as the reaction progressed did not display any shift in wavelength of maximum absorption. (c) Lack of anions and cations catalysis which might be because, the rate-determining step in reactions involved dissociation of the oxidant intermediates. These species are likely to exhibit little or no interaction with the added ions.

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Compliance with Ethical Standards

Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable.

Availability of data and materials

The publisher has the right to make the data public.

Competing interests

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All the authors contributed to the benchwork and the reporting of the work. ASJ designed the work while the experimental aspect of the work and the reporting were jointly carried out by ASJ, IBA and IEO