KINETICS AND MECHANISM OF REDOX REACTION OF TETRAKIS (2, 2'- BIPYRIDINE)-µ- OXODIIRON (III) COMPLEX AND GLUTATHIONE IN AQUEOUS HYDROCHLORIC ACID

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Abstract: Redox reaction of tetrakis(2,2'- bipyridine)-µ-oxodiiron(III) complex, Fe_2O^{4+} and glutathione (GSH) has been carried out in aqueous hydrochloric acid. The reaction was carried out at $[H^+] = 0.001$ mol dm^{-3}, $I = 0.3$ mol dm^{-3} (NaCl), T=27± 1°C, and λ_{max} = 520 nm. One mole of oxidant is consumed per mole of reductant. The reaction is first order with respect to $[Fe_2O^{4+}]$ and zero order on [GSH] and is not hydrogen ion and ionic strength dependent. Added anions and cations have no effect on the reaction; moreover there was no gel formation when acrylamide and excess methanol were added to the reaction mixture, which shows the absence of polymerization. With recourse to experimental data, the reaction is rationalised to follow outer sphere mechanism with ion pair character.

Keywords: Kinetics, mechanism, redox, glutathione, oxidant and reductant

Introduction

Glutathione (GSH) also known as γ-L-glutamyl-L-cysteinyl-glycine is a thiol with -SH functional group at cysteine. GSH is required for several cell processes interconnected with alterations in the maintenance and regulation of the thiol-redox status, due to its capability to exist in different redox specie (Forman *et al.,* 2009). GSH is a major antioxidant in the brain (Dringen, 2000), with a concentration which is much higher than that in blood or cerebrospinal fluid (Cooper and Kristal, 1997). It exerts its functions via several mechanisms. First, GSH non-enzymatically reacts with superoxide (Winterbourn and Metodiewa, 1994), NO (Clancy, 1994), hydroxyl radical (Bains and Shaw, 1997), and $ONOO^-$ (Koppal *et al.,* 1999).

In particular, GSH has a higher ability to scavenge superoxide than cysteine (Hussaini *et al.,* 1996). Furthermore, there is no known enzymatic defense against hydroxyl radicals, making GSH the only compound capable of scavenging these radicals (Bains and Shaw, 1997). GSH also serves as an essential cofactor for a number of enzymes. It works as an electron donor for the reduction of H_2O_2 or other peroxides catalysed by glutathione peroxidases (Chance *et al.,* 1979). The brain has a relatively high level of glutathione peroxidases as compared with that of catalase, while the liver has high levels of both (Maher, 2005). GSH reacts with various endogenous and xenobiotic compounds mediated by glutathione-S-transferase (GST) (Commandeur*et al.,* 1995) to form mixed disulphides, which are exported to the outside of the cell. GSH can also react with 4-hydroxynonenal via the action of GST to form the GSH-hydroxynonenal adduct (Xie *et al.,* 1998). This process plays an important role in cellular detoxification. Moreover, GSH is the major redox buffer and maintains intracellular redoxhomeostasis. Under conditions of oxidative stress, GSH can lead to the reversible formation of mixed disulphides between protein thiol groups (S-glutathionylation), a process critical for preventing irreversible oxidation of proteins (Giustarini *et al.,* 2004). GSH is thought to exert dual (agonistic/antagonistic) actions on neuronal responses mediated by NMDA receptors in the brain. GSH also serves as an endogenous NO reservoir to form S-nitrosoglutathione (Singh *et al.,* 1996).

The chemistry of diiron complexes for the past decades have continued to be of great interest because of the presence of such diiron centres in a variety of non-haem iron proteins. Participation of the *µ*-oxo diiron cores of the metalloproteins, hemerythrin, ribonucleotide reductase, and purple acid phosphatase in their biological oxygen-transport and oxygenation processes is well known (Stenkamp *et al.,* 1981; Anatanaitis and Aisen, 1983; Sjoberg and Graslund 1983; Wilkins and Harrington, 1983; Sheriff *et al*., 1987). Though the diiron complexes have been known for long, to a large extent, greater focus was on their synthesis and characterisation. Numerous diiron(III) complexes have been prepared and characterised using several spectroscopic techniques such as infrared, UV-visibe and nuclear magnetic resonance (Gaines *et al.,* 1936; Schugar *et al.,* 1967, 1969; Reiff *et al.,* 1968; David *et al.,* 1972; Reiff, 1977; Nozaki *et al.,* 1999).

In view of the roles GSH, as enumerated above, there is need for kinetic data of the electron transfer of this important biochemical with tetrakis (2,2´- bipyridine)**-µ-** oxodiiron(III) complex. The kinetic data generated from the electron transfer reaction between the biochemical compound and Fe_2O^{4+} will complement the much needed kinetic information and will bring to the limelighttheir electron transfer properties.

Materials and Methods

Experimentals

Materials

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 characterized following the method of (David, 1973). A stock solution of GSH (Sigma−Aldrich) was prepared by dissolving appropriate quantity of GSH into distilled water in volumetric flask and made up to the mark. 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 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 sulphate, sodium acetate, 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 λ_{max} = 520 nm using the mole ratio method (Ukoha and Iyun, 2001, 2002). The concentration of Fe_2O^{4+} was kept constant at 6.7 x 10^{-5} mol dm^{-3} while that of GSH was varied between (2.68 – 29.5) x 10^{-5} mol dm^{-3} at $[H^+] = 1.0$x 10^{-3} mol dm^{-3} and constant ionic

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strength of 0.3 mol dm $^{-3}$(NaCl) at T = 27 ±1.0ºC. The reactions were allowed to stand until the repeated absorbances of the reaction mixture at λ_{max} = 520 nm were constant. The stoichiometry was then determined from the plot of absorbance versus mole ratio of Fe_2O^{4+}: GSH.

Kinetic studies
The rate of reaction was studied under pseudo-first order condition with [GSH] 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 525. From the slopes of pseudo-first order plots of log (A_∞ - A_t) versus time, the pseudo-first order rate constant (k_1) were determined.

Acid dependence studies
The effect of changes in the hydrogen ion concentration 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}.

Effect of ionic strength
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.

Influence of added anions
The influence of added sulphate and acetate ions on the rate of reaction were investigated by varying the concentration of these anions whilekeeping [Fe_2O^{4+}], [GSH] 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$^+$], I and temperature. Any polymerisation as indicated by gel formation suggested the presence of free radicals in the reaction mixture (Iyun and Adegite, 1990; Vaidya *et al.,* 1991).

Products analysis
At the completion of the reaction, the reaction mixtures were analysed for the type of organic and inorganic products formed. The test for the presence of disulphide was carried out according to literature (McAuley and Gomwalk, 1968, 1969). The GSHreacted with a little excess of the oxidant in acid medium and ionic strength of reaction. At the completion of the reaction, the mixture was extracted six times with diethyl ether. The combined ether extracts were washed and dried with anhydrous Na$_2$SO$_4$ and left overnight to dry.

RESULTS AND DISCUSSION
Stoichiometric studies showed that one mole of Fe_2O^{4+} is reduced per two moles of GSH oxidised. The overall reactions can be represented in equation 1.
$$Fe_2O^{4+} + 2GSH \rightarrow 2Fe^{2+} + GSSG + H_2O \qquad 1$$
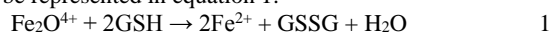
The stoichiometry of 1:2 (oxidant: reductant) is in agreement with the report given by other authors as follows: Ru_2O^{4+} with glutathione (Ayoko *et al*., 1993), Iron(III)-2,2`-bipydridyl withmethionine (Tiruveedhula *et al*., 1995), Ru_2O^{4+} with L-cysteine (Iyun *et al*., 1996), $[(FeHEDTA)_2O]^{2-}$ with mercaptoacetic acid, mercaptoethylamine and mercaptoethanol (Ukoha, 1999; Ukoha and Iyun, 2001). However, this mole ratio is not analogous to 1:1 (oxidant: reductant) reported foroxidation ofmercaptoacetic acid by 12-tungstocobaltate(III) (Ayoko, 1981; Ayoko and Olatunji, 1983), tris (polypyridyl) iron(III) complex with glutathione (Ayoko *et al.,* 1993), reaction oftrisoxalatocobaltate(III) iron with mercaptoacetic acid

(Lawal *et al.,* 1994),Ru_2O^{4+} with mercaptoethylamine and mercaptoethanol (Iyun *et al.,* 1995c), Ru_2O^{4+} with mercaptoacetic acid (Musa *et al.,* 1998), oxidation of mercaptoacetic acid and L-cysteine by Fe_2O^{4+} (Idris *et al.,* 2004; Idris, 2005).

Tiruveedhula *et al.* (1995) reported that the oxidation of many thiols can give rise to many products depending on the nature of the oxidant. Methionine and mercaptobenzoic acid were oxidised to sulphoxide by oxidants such as chlorocauric acid, Cr(IV), hexachloroiridate sulphite, iron (III) -2, 2'-bipyridyl and Mn^{II}O$_2$M^{IV} (Natile *et al.,* 1976; Goswami *et al.,* 1981; Olatunji and Ayoko, 1988; Ayoko *et al.,* 1992; Tiruveedhula *et al.,* 1995; Lohdip, 1999). In the reaction of Fe_2O^{4+} with mercaptoacetic acid and L-cysteine, derivative of sulphonic acid was obtained as the organic product (Idris *et al.,* 2004; Idris, 2005). However disulphide (GSSG) was formed asthe only organic product in the reactions and this was confirmed using the method of McAuley and Gomwalk (1968 and 1969). Subsequently the crystals obtained from the above method was subjected to FTIR spectroscopy to authenticate the formation of disulphide (GSSG). The weak absorption at $V(542)cm^{-1}$ confirmed the formation of disulhpide (GSSG). Disulphide formation has been observed in the reactions of Ru_2O^{4+} with L-cysteine (Iyun *et al.,* 1996), and mercaptoacetic acid (Musa *et al.,* 1998) and $[(FeHEDTA)_2O]^{2-}$with mercaptoacetic acid, mercaptoethanol and mercaptoethylamine (Ukoha 1999; Ukoha and Iyun, 2001). Addition of K$_3$[Fe(CN)$_6$] to the products of the systems gave a blue black colour which depict the presence of Fe^{2+} as an inorganic product.

Kinetic studies of the reduction of Fe_2O^{4+} by GSH indicated first order dependence on the [Fe_2O^{4+}]. Pseudo-first order plots of $\log(A_\infty - A_t)$ versus time were linear (Fig. 1) for about 85% extent of reaction. The invariance of k$_{obs}$ in Table 1 indicated zero order dependence on the [GSH]. The rate of redox process can therefore be represented as;
$$\frac{1}{2}\frac{d[Fe^{2+}]}{dt} = k_{obs}[Fe_2O^{4+}] \qquad (2)$$

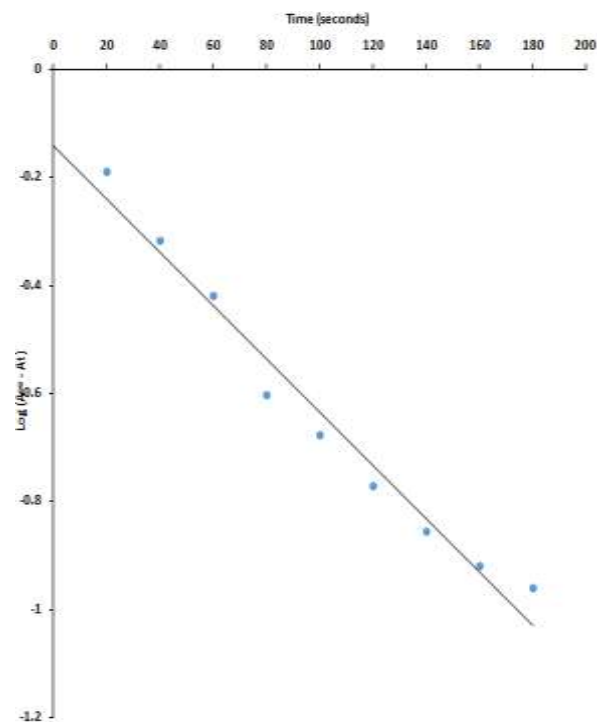**Fig. 1: Typical Pseudo-first order plot for the redox reaction of $Fe_2O^{4+}$with GSH at [Fe_2O^{4+}] = 2.0 × 10⁻⁴ mol dm⁻³, [GSH] = 5.0 × 10⁻³mol dm⁻³, [H⁺] = 1.0 × 10⁻³ mol dm⁻³, I = 0.30 mol dm⁻³ (NaCl), T = 26.0 ± 1.0ºC and λ$_{max}$ = 520 nm**

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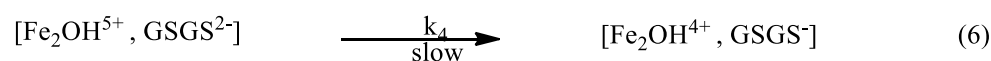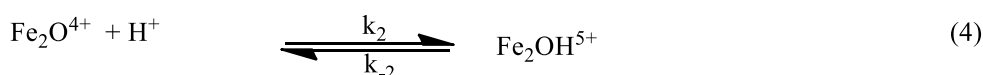
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Table 1: Pseudo-first order rate constants for the redox reaction of Fe_2O^{4+} – GSH in aqueous HCl medium, λ_{max} = 520 nm, I = 0.30 mol dm^{-3} (NaCl), [Fe$_2$O^{4+}] = 5 × 10^{-5} mol dm^{-3}, T = 26.0 ±1.0°C

10^3[GSH] (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	4.32
4.0	1.0	3.0	3.92
6.0	1.0	3.0	4.10
8.0	1.0	3.0	4.08
12.0	1.0	3.0	4.01
14.0	1.0	3.0	4.01
16.0	1.0	3.0	3.89
6.0	0.4	3.0	4.13
6.0	0.6	3.0	4.36
6.0	0.8	3.0	4.24
6.0	1.0	3.0	4.40
6.0	1.2	3.0	3.87
6.0	1.4	3.0	4.23
6.0	1.0	1.0	3.60
6.0	1.0	2.0	4.12
6.0	1.0	3.0	4.10
6.0	1.0	4.0	3.70
6.0	1.0	5.0	3.70
6.0	1.0	6.0	4.01

The zeroth order with respect to [GSH] is similar to what was obtained in the reduction of Fe_2O^{4+} by mercaptoacetic acid and L-cysteine (Idris, 2005). However, this result does not conform to the result from earlier researchers. For instance, first order dependence were observed on both [reducant] and [oxidant] in the oxidation of mercaptoethanol, mercaptoethylamine and mercaptoacetic acid by Ru_2O^{4+} (Iyun *et al.,* 1995c; Musa *et al.,* 1998) and $[(FeHEDTA)_2O]^{2-}$ (Ukoha, 1999; Ukoha and Iyun, 2001), in the reactions of Cr(VI) with L-cysteine (Iyun andTinounye, 1998), mercaptoacetic acid by IO_3^- (Ukoha and Ibrahim, 2004) and mononuclear Fe(III) with thiols (Wiberg *et al.,* 1968).

Within the acid range of $(4.0 - 14) \times 10^{-4}$ mol dm^{-3} the rate of reaction displayed non- dependence on [H$^+$] in the reaction ofFe_2O^{4+} and GSH. Similar report has been posited

in the reaction of the oxidant (Fe$_2$O^{4+}) with mercaoptacetic acid and L-cysteine (Idris, 2005). On the other hand, increased in reaction rate with increase in [H$^+$] has been reported in the reaction of thiols with trisoxalatocobaltate(III) ion (Lawal *et al*., 1994) and trispolypyridyl iron(III) complexes (Ekubo, 1992; Ayoko *et al.,* 1993a, b), also inverse acid dependence in thiols reaction with Ru_2O^{4+} (Ayoko *et al.,* 1993; Iyun *et al.,* 1995, 1996; Musa *et al.,* 1998), iron(III)-2,2'-bipyridyl (Tiruveedhula *et al.,* 1995), Cr(VI) (Iyun and Tinouye 1998), and $[(FeHEDTA)_2O]^{2-}$ (Ukoha, 1999; Ukoha and Iyun, 2001) have been reported. Varying the ionic strength of the reaction media between 0.1 – 0.6 mol dm^{-3} (NaCl), had no effect on the rates of reaction. Change in the dielectric constant of the medium did not affect the rate of the reaction as well. Similar observation with respect tothe effect of ionic strength and dielectric constant on the reaction rate have been noticed in the reaction of $[(FeHEDTA)_2O]^{2-}$ with mercaptoethylamine and mercaptoethanol (Ukoha and Iyun, 2001) and Fe_2O^{4+} with mercaptoacetic acid and L-cysteine (Idris, 2005). Nonetheless reactions of mercarptoacetic acid and L-cysteine with Ru_2O^{4+} (Iyun *et al.,* 1996; Musa *et al.,* 1998) decreased with increase in ionic strength. Also there was a marked enhancement of the rate of these reactions as a function of 1/D, both of these features posited that, the rate determining step involved oppositely charged redox species.

Free radical test was carried out by addition of acrylamide to the reaction mixtures, followed by excess methanol, there was no gel formation, suggesting that polymerisation has not occurred. Lack of polymerization from this reaction suggests probable absence of free radical formation during the electron transfer. On the other hand, free radical could have been formed but reacts so quickly that this method could not detect it (Iyun *et al.,* 1995). The rate of reaction was not affected by added cations and anions.. Absence of spectroscopic evidence for the formation of intermediate during the reaction suggests that a precursor complex is probably not formed prior to the act of electron transfer and that the electron transfer may occur by the outer-sphere path. With recourse to the empirical kinetic data, the mechanism of this reaction is proposed as follows:

$$2GSH \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad [GSH.GS^-] + H^+ \qquad (3)$$

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

$$Fe_2OH^{5+} + [GSH.GS^-] \quad \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad [Fe_2OH^{5+}, GSGS^{2-}] + H^+ \qquad (5)$$

$$[Fe_2OH^{5+}, GSGS^{2-}] \quad \underset{slow}{\overset{k_4}{\longrightarrow}} \quad [Fe_2OH^{4+}, GSGS^-] \qquad (6)$$

$$[Fe_2OH^{4+}, GSGS^-] \quad \overset{k_5}{\longrightarrow} \quad Fe_2OH^{3+} + GSSG \qquad (7)$$

$$Fe_2OH^{3+} + H^+ \quad \overset{k_6}{\longrightarrow} \quad 2Fe^{2+} + H_2O \qquad (8)$$

$$Rate \quad = \quad k_4[Fe_2OH^{5+}, GSGS^{2-}] \qquad (9)$$

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Application of steady state hypothesis for $[Fe_2OH^{5+}, GSGS^{2-}]$ gives:

$$[Fe_2OH^{5+}, GSGS^{2-}] = \frac{k_3[Fe_2OH^{5+}][GSH.GS^-]}{k_{-3}[H^+] + k_4} \qquad (10)$$

If $k_{-3}[H^+] \gg k_4$ equation 10 reduces to

$$[Fe_2OH^{5+}, GSGS^{2-}] = \frac{k_3[Fe_2OH^{5+}][GSH.GS^-]}{k_{-3}[H^+]} \qquad (11)$$

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

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2O^{4+}][H^+]}{k_{-2} + k_3[GSH.GS^-]} \qquad (12)$$

From equation 12, if $k_{-2} \ll k_3[GSH.GS^-]$, then the equation reduces to:

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2O^{4+}][H^+]}{k_3[GSH.GS^-]} \qquad (13)$$

Substituting equation 13 into 11 gives:

$$[Fe_2OH^{5+}, GSGS^{2-}] = \frac{k_3 k_2[Fe_2O^{4+}][H^+][GSH.GS^-]}{k_{-3}[H^+]\, k_3[GSH.GS^-]} \qquad (14)$$

$$[Fe_2OH^{5+}, GSGS^{2-}] = \frac{k_2}{k_{-3}}[Fe_2O^{4+}] \qquad (15)$$

Substituting equation 15 into 9 gives:

$$\text{Rate} = \frac{k_4 k_2}{k_{-3}}[Fe_2O^{4+}] \qquad (16)$$

$$\text{Thus } \frac{k_4 k_2}{k_{-3}} = k_{obs} \qquad (17)$$

Conflict of Interest
Authors declare that there is no conflict of interest related to this work.

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