Mechanism of Electron Transfer Reaction between L-cysteine and tetrakis(2,2'-bipyridine)-μ-oxodiiron (III) ion in Aqueous Acidic Medium

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Abstract

Oxidation of L-cysteine by tetrakis(2,2'-bipyridine)-μ-oxodiiron (III) ion has been investigated in aqueous acidic medium by measuring increase in the absorbance of the product solution at 520nm. The reaction displayed 1:1 stoichiometry and obeyed the rate law:

$$\frac{1}{2}\frac{d[Fe^{2+}]}{dt} = k_{obs}[Fe_2O^{4+}]$$

The rate of the reaction was independent of changes in ionic strength and dielectric constant of the reaction media. The outersphere mechanism is suggested for this reaction.

Keywords: Kinetics, mechanism, L-cysteine, tetrakis(2,2'-bipyridine)-μ-oxodiiron (III) ion, outersphere.

Introduction

Oxobridged binuclear complexes of iron (III) provide good examples of Robin and Day classification of transition metal complexes where two metal centres linked by bridging ligand differ significantly in terms of metal-metal electronic interactions [1]. Recently, reactions of these complexes are being followed with keen interest as they could possibly provide a better understanding of the respiratory processes in mammals and some haem proteins [2-9].

L-cysteine, an essential amino acid and also a thiol is of biochemical interest. It

serves as reactivator of fibrin stabilizing factor form an otherwise dormant form in blood clothing [10]. Literature has shown that in the oxidation of thiols, binuclear complex formation may [11,12] or may not by important [2,4,13]. Part of the motivation for this study is to find out which of the above mechanistic options is adopted by the reaction of interest. We here in report the mechanism of the electron transfer reaction between L-cysteine and tetrakis(2,2'-bipyridine)-μ-oxodiiron(III) ion in aqueous acidic medium.

Experimental

Detailed procedures for the preparation and standardization of the oxobridged compound, $[(bpy)_2ClFe-O-FeCl(bpy)_2]Cl_4$ (where bpy is bipyridine) were described previously [9]. For convenience, we represented the ion of this complex by Fe_2O^{4+} throughout the text. On the other hand, L-cysteine hydrochloride (M&B) was designated as GSH and solutions of this were freshly prepared when required. HCl (M&B) was used to probe effect of $[H^+]$ on the reaction rate while NaCl was used to maintain the ionic strength, μ, of reaction medium constant at 0.01 mol dm^{-3}. All the reagents used were of analytical grades and were used without further purification except otherwise stated.

Using different concentrations of reductant in the range 1.6 x 10^{-5} to 10 x 10^{-5} mol dm^{-3} and $[Fe_2O^{4+}]$ = 4 x10^{-5} mol dm^{-3} at μ = 0.05 mol dm^{-3}, $[H^+]$ = 6 x 10^{-5} mol dm^{-3} and T= 30ºC, the stoichiometry of the reaction was investigated [9]. The reaction rate was determined by following increase in the absorbance of the product solution using Chroma 254 Digital Colorimeter at 520 nm after having certified that none of the reactants absorbed at this wavelength. Pseudo-first order conditions were employed with the [GSH] in at least 30-fold excess over that of $[Fe_2O^{4+}]$. Dielectric constant of the reaction medium (D) was investigated as reported earlier [9].

NO^-_3 and ClO_4^- were used to investigate the possible catalysis of the reaction of interest. Presence of free radicals was determined by adding acrylamide to partially reacted mixture in excess the methanol.

Result and Discussion

Stoichiometric study indicated that for each mole of GSH oxidized, one mole of the complex, Fe_2O^{4+} is reduced in accordance with equation (1).

$$Fe_2O^{4+} + GSH + O_2 \rightarrow 2Fe^{2+} + GSO_3H \qquad (1)$$

The formation of sulphonic acid derivative as organic product of this reaction was confirmed by the similarity between the uv spectra of this product solution and that of the product solution and the that of the product solution of GSH and concentrated trioxonitrate (V) acid. Strong oxidants such as concentrated trioxonitrate (V) acid and

$KMnO_4$ oxidize thiols to the corresponding sulphonic acid derivatives [14]. In principle, oxidation of GSH can occur via N. O or S. The above result shows that electron transfer occurred more readily at S atom, S being more nucleophilic than N or O. The inorganic product of the reaction, Fe^{2+} was identified spectroscopically [9].

Pseudo-first order plots of log (A_∞ -A_t) against time (where A_∞ and A_t are absorbances at the end of the reaction and at time, t respectively) were linear to about 20% extent of reaction. In line with the previous investigation, the deviation from linearity suggests product inhibition [15]. The observed rate constants (k_{obs}) were evaluated from the slopes of the initial points on the curves. The invariance of k_{obs} in Table 1, suggest zero order dependence on [GSH]. The rate of the reaction can therefore be represented by equation 2.

$$\frac{1}{2}\frac{d[Fe^{2+}]}{dt} = k_{obs}[Fe_2O^{4+}] \tag{2}$$

At fixed $[Fe_2O^{4+}]$, [GSH], $[H^+]$ and temperature, the rate of the reaction was constant, with increase in ionic strength of the reaction medium (Table 1). This is an indication that the product of the charges on the activated complex is zero [16]. Alternatively, there is active participation ion-pair in the rate determining step [17]. These views are reinforced by the non-dependence of the rate of the reaction on the dielectric constant of the reaction medium (Table 2).

Table 1: Pseudo–first order rate constants for the reaction of Fe_2O^{4+} and L– cysteine (GSH) at $[Fe_2O^{4+}] = 6.67 \times 10^{-5}$ mol dm^{-3}, $\lambda_{max} = 520$ nm and T = 30°C.

10^4[GSH],mol dm^{-3}	10^6[H$^+$],mol dm^{-3}	$10^2\mu$,mol dm^{-3}	$10^3 k_{obs}$,s^{-1}
21.30	60	10	6.35
28.0	60	10	6.06
34.70	60	10	6.16
41.30	60	10	6.18
48.0	60	10	6.14
28.0	10	10	6.14
28.0	40	10	6.64
28.0	80	10	6.20
28.0	120	10	6.20
28.0	160	10	6.28
28.0	200	10	6.28
28.0	60	5	6.20
28.0	60	10	6.14
28.0	60	15	6.04
28.0	60	20	6.14
28.0	60	25	6.14

Table 2: Dependence of rate constants on anions (X) and on dielectric constant (D) of the reaction medium for the reaction of Fe_2O^{4+} and L–cysteine(GSH) at $[Fe_2O^{4+}]$ = 6.67 x 10^{-5} mol dm^{-3}, [GSH] =28 x 10^{-4} mol dm^{-3},$[H^+]$ = 6 x 10^{-5} mol dm^{-3}, μ = 0.01mol dm^{-3}, λ_{max} = 520 nm and T = 30°C.

X	$10^4[X]$,mol dm^{-3}	$10k_{obs}$,s^{-1}
NO_3^-	20	6.28
	60	6.21
	100	6.28
	120	6.28
ClO_4^-	20	6.14
	40	6.05
	60	6.21
	120	6.05
D		
81		6.05
80.2		5.08
79.4		5.25
74.6		5.23

Fe_2O^{4+} was unstable in $[H^+]$ greater than 10^{-4} mol dm^{-3}, hence kinetic studies was limited to $1x10^{-6} \leq [H^+] \leq 2x10^{-4}$ mol dm^{-3}. Lack of H^+ dependence on reaction rate has characterized this reaction in the range indicated in Table 1. We have earlier reported similar observation in the reactions of the oxidant with organic [5,7,9] and inorganic (6) substrates.

Based on the above results, the following mechanistic scheme is proposed for the reaction.

$$Fe_2O^{4+} + H^+ \underset{k}{\overset{k_1}{\rightleftharpoons}} Fe_2OH^{5+} \tag{3}$$

$$Fe_2OH^{5+} + GSH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe_2OH^{5+}, GS^-] + H^+ \tag{4}$$

$$[Fe_2OH^{5+}, GS^-] \xrightarrow{k_3} Fe_2O^{3+} + GS + H^+ \tag{5}$$

$$Fe_2O^{3+} + GS + H^+ + O_2 \xrightarrow{k_4} 2\,Fe + GSO_3H \tag{6}$$
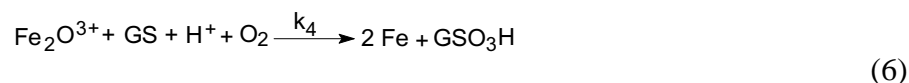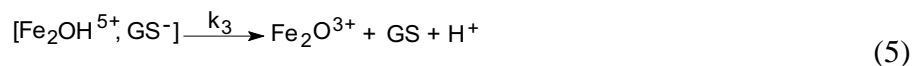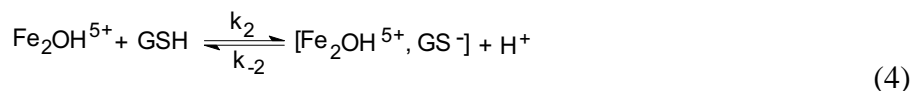
$$Rate = k_3 [Fe_2OH^{5+}, GS^-] \tag{7}$$

According to steady state hypothesis,

$$[Fe_2OH^{5+}, GS^-] = \frac{k_2[Fe_2OH^{5+}][GSH]}{k_3 + k_{-2}[H^+]}$$

(8)

Substitution of equation (8) into (7) gives

$$Rate = \frac{k_2k_3[Fe_2OH^{5+}][GSH]}{k_3 + k_{-2}[H^+]}$$

(9)

But

$$[Fe_2OH^{5+}] = \frac{k_1[Fe_2OH^{4+}][H^+]}{k_{-1} + k_2[GSH]}$$

(10)

Equation (9) reduces to (11) after substituting (10) into (9).

$$Rate = \frac{k_3k_2k_1[Fe_2O^{4+}]}{(k_3 + k_{-2}(k_{-1} + k_2)}$$

(11)

Equation (11) is similar to equation (2) where:

$$\frac{k_3k_2k_1}{(k_3 + k_{-2})(k_{-1} + k_2)} = k_{obs}$$

The pathway for this reaction can be addressed by considering the following points.

a. Absence of spectrophotometric evidence for the presence of intermediates when partially reacted mixture was scanned shows that a precursor complex is probably not formed prior electron transfer step.

b. Direct bond formation between Fe moiety and GSH would involve destruction of Fe-O-Fe framework and is therefore unlikely, an indication that presence of binuclear intermediate is remote. In this vein, the reaction of Fe_2O^{4+} resembles that of Ru_2O^{4+} with L-cysteine and mercaptoacetic acid where the reactions were suggested to occur by outersphere mechanism [18,19].

c. The views in (a) and (b) point to the outersphere mechanism. However, there is absence of anions catalysis (Table 2). This is expected because the rate determining step (equation 5) is characterized by dissociation of the ion-pair complex. This species is not likely to interact with added anions.

The above point is in favour of the outersphere mechanism and is hereby proposed for the title reaction.

Acknowledgement

References

[1] Robin, M.B., Day, P., 1967, Mixed valence chemistry. A survey and classification. Adv. Inorg. Chem. Radiochem., 10 pp. 247.

[2] Ukoha, P.O., Iyun, J.F., 2001, Kinetics of the oxidation of 4,4-(phenylemethylene)b is(N,N-dimethylbenzenamine)(leucomalachite green) by Cr(VI) in aqueous acid media.J.Chem.Soc.Nig., 26(2) pp. 163.

[3] Ukoha, P.O., Iyun, J.F., 2002, Oxidation of L-ascorbic acid by enH$_2$[(FeHEDTA)$_2$O.6H$_2$O in aqueous medium. J Chem Soc.Nig., 27(2), pp. 119.

[4] Ukoha, P.O., Iyun, J.F., 2005, Mechanism of the oxidation of 2-mercaptoacetic acid by enH$_2$[(FeHEDTA)$_2$O.6H$_2$O in aqueous medium Chemclass J., pp. 51.

[5] Idris, S.O., Iyun, J.F. Agbaji, E.B., 2004, Kinetics and mechanism of the oxidation of catechol by Fe$_2$(bipy)$_4$O^{4+} in aqueous hydrochloric acid medium. ChemClass J., pp. 27.

[6] Idris, S.O., Iyun, J.F. Agbaji, E.B., 2005, Kinetics and mechanism of the reduction of trioxoiodate(V) ion by 1,2-dihydroxybenzene in aqueous hydrochloric acid medium.ChemClass J., pp. 85.

[7] Idris, S.O., Iyun, J.F. Agbaji, E.B., 2007, Kinetics of the reduction of tetrakis (2,2'-bipyridine)-μ-oxodiiron(III) ion by mercaptoacetic acid in aqueous hydrochloric acid medium Afr. J. Nat. Sci., 10, pp. 35.

[8] Idris, S.O., Iyun, J.F. Agbaji, E.B. 2008, Kinetics and mechanism of the oxidation of thiosulphate by tetrakis (2,2'-bipyridine-μ-oxodiiron (III) in aqueous acidic medium. Ife J. Sci.,10(1), pp. 103.

[9] Idris, S.O., Iyun, J.F. Agbaji, E.B., 2009, Kinetics of the reduction of tetrakis(2,2'-bipyridine)-μ-oxo-di-iron(III) by 1,3-benzenediol in aqueous acid medium. Transition Met.Chem, 34, pp. 205.

[10] Lorand, L., Jacobson, A., 1958, Biogenesis of protein fibre. The clothing of plasma. J.Biol.Chem, 230, pp. 421.

[11] McCann, J.P., McAuley, A., 1958, Metal ion oxidation in solution. The reaction of chromium (VI) with L-cysteine in perchlorate media. J.Chem.Soc, A, pp. 783.

[12] Iyun, J.F., Tinuoye, E.O., 1998, Chromium (VI) oxidation of L-cysteine. ChemClass Conf.Proceeding, pp. 56.

[13] Ayoko, G.A., Olatunji, M.A., 1983, Oxidation of L-cysteine, mercaptoacetic acid and β-mercaptoethylamine by 12-tungstocobaltate (III). Polyhedron, 2, pp. 577.

[14] Streiwieser, A., Heathecock, C.H., 1985, 'Introduction to organic chemistry', 3rd Ed., Macmillan Publishing Company New York and Cotheir Macmillan Publishers; London.

[15] Iyun, J.F., 2004, The oxidation of some tris(diimine)iron (II) and tris(substituteddiimine) iron (II) complexes by aqueous acidic bromine solution. An assessment of thev marcus model for non-complimentary reactions. ChemClass J., pp. 59.

[16] Atkins, P., de Paula, J.2002, 'Physical Chemistry' 7th Ed., Oxford University Press.

[17] Iyun, J.F., Musa, K.Y., Ayoko, G.A., 1995, Oxidation of 2-mercaptoethanol and 2-mercaptoethylamine by $[(bpy)_2H_2ORU \quad]_2O^{4+}$ in aqueous media. Indian J.Chem. 34A, pp. 635.

[18] Ayoko, G.A. Iyun, J.F. Mamman, S.1993, Kinetics and mechanism of the oxidation of nitrolotriacetate by poly(pyridyl)iron(III) complexes and catungstocobaltate(III). Indian J.Chem, 32A, pp. 1089.

[19] Musa, K.Y., Iyun, J.F., Ayoko, G.A., 1995, Oxidation of 2-mercaptoethanol and 2-mercaptoethylamine by $[(bpy)_2H_2ORU \quad]_2O^{4+}$ in aqueous media. Bull.Sci.Assoc.Nig, 19, pp. 212.