**Kinetics and Mechanism of the Reduction of N-(2-Hydroxyethyl)ethylenediaminetriacetatoiron(III) Complex by Thioglycol in Bicarbonate Buffer Medium**

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**ABSTRACT**

The kinetics and mechanism of reduction of N-(2-hydroxyethyl)ethylene- diaminetriacetatoiron(III) complex (hereafter [Fe(III)HEDTAOH2]) by thioglycol (hereafter RSH) has been studied spectrophotometrically in a bicarbonate buffer medium. The study was carried out under pseudo-first order conditions of an excess of thioglycol concentration at 28 ± 1$℃$, I = 0.44 mol dm-3 (KNO3) and *λ*max = 490 nm. The reaction is first order in [Fe(III)HEDTAOH2] and half order in [RSH] and a stoichiometric mole ratio of [Fe(III)HEDTAOH2] : RSH is 2:1. Reaction rates increased with increase in ionic strength (I) and dielectric constant (D) of the reaction medium of the reaction. The reaction displayed positive primary salt effect which suggests the composition of activated complex are likely charged reactants ions. Test for possibility of an intermediate complex formation shows negative as Michaelis-Menten plot was linear with very negligible intercept. Based on the findings, outer-sphere mechanism is proposed for the reaction. The experimental rate law obtained is;

$\frac{d[Product]}{dt}$ = k2[Fe(III)HEDTAOH2][RSH]1/2

Keywords:Kinetics, N-(2-hydroxyethyl)ethylenediaminetriacetatoiron(III) Complex, Mechanism, Thioglycol, Reduction

**1. Introduction**

The kinetic studies of electron transfer reactions of thioglycol have recorded much interest since it has been employed to act as a biological antioxidant by scavenging hydroxyl radicals (Aitken, et al., 2008). Thioglycol undergoes electron transfer reaction by deprotonation and loss of one electron in mostly alkaline media. It has wide application in preventing protein oxidation (Verdugn et al., 1985), denaturing of ribonucleases (Nelson et al., 2015) and reducing proteins (Stevens et al., 9183). The reactions of this substrate have been of interest. The review of its oxidations with different substrates (Chakraborty and Banerjee, 2014; Chakraborty et al., 2012; Shanmugaprabha et al., 2016; Chakraborty et al., 2013; Goswami et al., 2003) and its dimerization to form disulfide in biological systems have been studied (Messmore et al., 2000). Equally, kinetics study on the reduction of Fe(III) aminocarboxylates complexes (Wang et al., 2008; Balahura and Johnson, 1987; Buettner et al., 1983; Xiao-juan et al., 2011; Francis et al., 1985; Bull et al., 1983; Suchecki et al., 2014; Mshelia et al., 2014; Dellert-Ritter and Eldik, 1992) by various reducing substrates have been scantly recorded.

The basis of this study is centered on the electron transfer reaction of this oxidant, and the quest to provide additional kinetic data that will shed more light on the pathway of the reaction in terms of Taube’s inorganic electron transfer reaction mechanistic classification.

**2. Experimental details**

The [Fe(III)HEDTAOH2] complex was prepared according to the method of Xiao-juan et al.*,* 2011 and was characterized using UV/Visible. The UV/Visible spectrum of [Fe(III)HEDTAOH2] was scanned between ranges of 300 – 700 nm and gave *λ*max of 360 and 490 nm.

N-(2-Hydroxyethyl)ethylenediaminetriacetatoiron(III) complex was prepared by adding standard solution of ferric nitrate (Sigma-Aldrich) and HEDTA (Sigma-Aldrich) in a ratio such that EDTA was in slight excess to ensure complete complexation. KNO3 (BDH) was used to maintain ionic strength. The complex stock solution had a concentration of about 0.05 mol dm-3. Prior to use, the solution’s pH is adjusted to 7.5 with bicarbonate buffer solution.

**2.1 Stoichiometric studies**

The stoichiometrywas determined by spectrophotometric titration using the mole ratio approach (Onu et al., 2016) under the reaction condition [Fe(III)HEDTAOH2] = 4.5 $×$ 10-3 mol dm-3, I = 0.1 mol dm-3, pH = 7.5, [RSH] = (0.9 – 11.7) $×$ 10-3 mol dm-3.

**2.2 Kinetic measurements**

The progress of the reaction rate was monitored under pseudo first order condition by observing change in absorbance of the reductant on Sherwood Colorimeter 254 at a λmax of 490 nm. The pH, temperature and ionic strength were kept constant. The plot of log (At - A∞) versus time using the first order rate equation

log(At - A∞) = $\frac{kt}{2.303}$ + log(At - A∞) (1)

was linear up to 90 % of the reaction (Fig. 1). The pseudo-first order rate constant, kobs, of the reaction was determined from the slope of the plot and are presented in Table 1. The log of kobs versus log [RSH] was plotted. Keeping all other reactions conditions constant as shown on (Tables 1 and 2), the influence of pH (6 – 10) and dielectric constant (75.5 – 80.1) and ionic strength (0.2 – 1.0) mol dm-3 using KNO3 was investigated for the reaction.

**2.3 The effect of added ion on the reaction rate**

The effect of added oxalate ion on the reaction was investigated at [C2O42-] = (1.0 – 21.0)$ ×$ 10-3 mol dm-3 while all other reactants concentration were kept were constant at I = 0.44 mol dm-3 (KNO3).

**2.4 Free radical test**

The investigation of participation of free radical was done by adding 3.00 cm3 of standard solution of acrylamide to a partially reduced reaction mixture containing various concentrations of oxidant and reductant and followed by addition of a large excess of methanol. The same treatment was applied to solution of reductant and oxidant separately.

**2.5 Temperature dependence**

The effect of temperature on the reaction rate was investigated to ascertain the thermodynamic parameters of the reaction medium by using Eyring’s plot of In (k2/T) versus 1/T, where in enthalpy of activation ∆H‡ is obtained from the slope, entropy of activation ∆S‡ is from the intercept. The Eyring’s equation is given as;

In (k2/T) = In (Kb/h) + ∆S‡/R - ∆H‡/RT (2)

**2.5 Product analysis**

The UV/Visible spectrum of the reaction product was scanned between wavelength ranges of 400 - 600 nm gave a λmax of 520 nm, which is characteristic of the Fe(II) product (Iyun, 2004; Idris et al., 2008), and the appearance of a red colour on addition of 1, 10- phenanthroline reveals the presence of Fe(II) product (Ellis et al*.,*1975). Investigation of the formation of sulfenic acid (RSOH) at the completion of the reaction was done by reducing the product with sodium ascorbate and sodium arsenite to thiol, which is confirmed by red colour formation when sodium nitroprusside or ammonium hydroxide is added to the test mixture (Saurin et al., 2004; Kettenhofen and Wood, 2010; Eaton, 2006; Gupta and Carroll, 2014).

**3. Results and discussion**

**3.1 Stoichiometry**

The spetrophotometric titrations showed oxidant - reductant ratio of 2:1 represented by the stoichiometric equation;

2[Fe(III)HEDTAOH2] + RSH → 2[Fe(II)HEDTA]- + RSOH + 2H+ + H2O (3)

Stoichiometry 2:1 obtained in this reaction has been documented with reaction involving thiol (Shi et al., 1996).

**3.2 Kinetic study**

The linearity of the pseudo-first order plots of log (At – A∞) versus time (Fig. 1) with 90 % extent of reaction indicates that the reaction is first order with respect to [Fe(III)HEDTAOH2]. The half order dependence with respect to [RSH] obtained is rationalized by the plot of log kobs versus log [RSH] having a slope of 0.55 (Fig. 2). Half order reaction as obtained with respect to the concentration of reductant is known to proceeds either by monomer-polymer equilibria with the monomeric species being the reactive form (Wilkins, 2002; Fawzy et al., 2017), or molecular dissociation (Berry et al., 1980; Onu et al., 2016). The redox reactions of first order dependence on [Fe(III)HEDTAOH2] have been reported (Buettner et al., 1983; Francis et al., 1985). Half order dependence on RSHas obtained for the [Fe(III)HEDTA(OH2)]/RSH reaction is uncommon, and it indicates the termination of the chance for the growth of a polymer chain that could has resulted to the formation of disulfide, but end up forming sulfenic acid, RSOH (Misra and Dubey, 1981).

**Table 1:** Pseudo-first Order and Second Order Rate Constants for the Reaction of

 [Fe(III)HEDTAOH2]and RSHat [Fe(III)HEDTAOH2] = 4.5 x 10–3 mol dm–3, I = 0.44 mol dm–3 (KNO3), pH = 7.5, T = 28 ± 1°C and λmax = 490 nm

102[RSH], mol dm-3 pH I, mol dm-3 103kobs, s-1 102k3/2, dm3/2 mol-1/2 s-1

1.0 7.5 0.44 1.25 1.00

2.0 7.5 0.44 1.97 1.00

3.0 7.5 0.44 2.53 1.07

4.0 7.5 0.44 2.92 1.09

5.0 7.5 0.44 3.26 1.12

6.0 7.5 0.44 3.52 1.11

7.0 7.5 0.44 3.76 1.12

8.0 7.5 0.44 3.99 1.13

7.0 6.0 0.44 12.21 4.61

7.0 6.5 0.44 3.87 1.46

7.0 7.0 0.44 4.03 1.52

7.0 7.5 0.44 3.57 1.35

7.0 8.0 0.44 5.53 2.09

7.0 8.5 0.44 8.28 3.13

7.0 9.0 0.44 13.73 5.19

7.0 9.5 0.44 10.48 3.96

7.0 7.5 0.30 2.67 1.01

7.0 7.5 0.40 3.64 1.38

7.0 7.5 0.50 4.87 1.84

7.0 7.5 0.60 6.48 2.45

7.0 7.5 0.70 7.95 3.00

7.0 7.5 0.80 8.04 3.04

7.0 7.5 0.90 8.35 3.14

7.0 7.5 1.00 8.36 3.15

**Fig. 1:** Typical Pseudo-first Order Plot for the Reaction of [Fe(III)HEDTAOH2] and RSH at [Fe(III)HEDTAOH2] = 4.5 × 10-3 mol dm-3, [RSH] = 7.0 × 10-2mol dm-3, I = 0.44 mol dm-3 (KNO3), pH = 7.5, T = 28 ± 1$℃$, and *λ*max = 490 nm

**Fig. 2:** Plot of log kobs versus log [RSH] for the Reaction of [Fe(III)HEDTAOH2] and RSHat [Fe(III)HEDTAOH2] = 4.5 × 10-3 mol dm-3, [RSH] = (1.0 – 8.0) × 10-2 mol dm-3, I = 0.44 mol dm-3 (KNO3), pH = 7.5, T = 28 ± 1$℃$, and *λ*max = 490 nm

**Fig. 3:** Plot log k2 versus √I for the Reaction of [Fe(III)HEDTAOH2] and RSHat [Fe(III)HEDTAOH2] = 4.5 × 10-3 mol dm-3, [RSH] = 7.0 × 10-2 mol dm-3, I = (0.2 – 1.0) mol dm-3, pH = 7.5, T = 28 ± 1$℃$, and *λ*max = 490 nm

**Fig. 4:** Plot of log kobs versus pH for the Reaction of [Fe(III)HEDTAOH2]and RSHat [Fe(III)HEDTAOH2] = 4.5 × 10-3 mol dm-3, [RSH] = 7.0 × 10-2 mol dm-3, I = 0.44 mol dm-3 (KNO3), T = 28 ± 1$℃$, and *λ*max = 490 nm

**3.2.1** **Effect of changes in ionic strength and dielectric constant of reaction medium on reaction rates**

The influence of ionic strength of the reaction medium by varying it from 0.3 – 1.0 mol dm–3 (KNO3) is positive on the rate constants of the reaction by increasing it (Table 1). This suggests the presence of charged ions at the activated complex. This is supported by the effect of changes in the dielectric constant, D, from 75.5 - 80.1 on the rates of the reaction. It was observed that the reaction rate increases with increased medium polarity.

**Table 2:** Effect of Changes in the Dielectric Constant of Reaction Medium on the Rate Constants for the Reduction of [Fe(III)HEDTAOH2] by RSHat [Fe(III)HEDTAOH2] = 4.5 × 10-3 mol dm-3, [RSH] = 7.0 × 10-2 mol dm-3, I = 0.44 mol dm-3 (KNO3), pH = 7.5, T = 28 ± 1$℃$, and *λ*max = 490 nm

**D 103kobs, s-1 102k3/2, dm3/2 mol-1/2 s-1**

80.1 3.76 1.42

79.5 3.64 1.38

78.9 3.12 1.18

78.4 2.98 1.13

77.8 2.74 1.04

77.2 2.05 0.77

76.7 1.96 0.74

76.1 1.36 0.51

75.5 1.26 0.48

**3.2.2 Effect of pH on reaction rates**

The investigation of pH-dependent on the reaction rate reveals that changes in pH (6.0 – 9.5) affected the reaction rate (Table 1), wherein there is a marked increase in the reaction rate at pH = 6.0, the dominance of the [Fe(III)HEDTAOH2] is expected, while at pH = 9.0, deprotonation can take place resulting to [Fe(III)HEDTA(OH)]- ion. Also, the rate-pH profile (Fig. 4) shows that both the ionized thiol (thiolate ion, RS-) and thiyl specie (RS**∙**) of the substrate are active species involved in the electron transfer, and non- participation of the hydroxyl specie of the complex in the redox process (Sami et al., 2009; Ghosh et al., 2013; Gangopadhyay et al., 1994).

**3.2.3 Effect of added oxalate ion on reaction rate**

There was positive Bronsted salt effect which can be accounted for by the interactions of the like charges in reaction.

**3.2.4 Detection of free radicals**

The polymerization test to ascertain the presence of active participation of free radicals in the reaction was positive as gelatinous precipitate was formed on the addition of acrylamide to partially reduced reaction mixture in excess methanol.

**3.2.5 Effect of temperature on reaction rates**

In temperature study with activation parameters (∆S‡ = -242.6 Jmol-1K-1, ∆H‡ = 8.15 kJmol-1 & ∆G‡ = 81.17 kJmol-1), the large negative value of entropy of activation clearly indicates the result of a large mutual ordering of solvated water molecules of equilibrium and electron transfer step. The values of enthalpy of activation and Gibbs free energy indicate the energy of formation associated with the precursor complex ([Fe(III)HEDTA(OH)]-) and the energy of intermolecular electron transfer step (Weaver and Yee, 1980).

**Fig. 5: Plot** of In(k2/T) versus 1/T for the Reaction of [Fe(III)EDTAOH2] and RSHat [Fe(III)EDTAOH2] = 4.5 x 10-3 mol dm-3, [RSH] = 7.0 x 10-2 mol dm-3, I = 0.44 mol dm-3 (KNO3), pH = 7.5$ $and λmax = 490 nm

**3.2.6 Michaelis-Menten plot**

Michaelis-Menten plot of 1/kobs versus 1/[RSH]1/2 was linear without any glaring intercept (Fig. 6). This confirms the absence of stable intermediate, but probably the formation of ion-pair (Osunlaji et al., 2012). The above findings support the suggestion that outer-sphere mechanism is operating in the reduction of the Fe(III) ion.

**Fig. 6:** Michaelis-Menten Plot of 1/kobs versus 1/[RSH]1/2 for the Reduction of [Fe(III)HEDTAOH2] by RSH

The empirical data is accounted for by the following mechanistic scheme which is in favor of the outer-sphere reaction.



Therefore,

Rate = k2[Fe(III)HEDTAOH- // RS-] + k4[Fe(III)HEDTAOH2 // RS.] (11)

From equation 6;

[Fe(III)HEDTAOH- // RS-] = k-1[Fe(III)HEDTAOH-][RS-] (12)

From equation 5;

[Fe(III)HEDTAOH-] = K2[Fe(III)HEDTAOH2] (13)

[H+]

Substituting equation 13 into equation 12;

[Fe(III)HEDTAOH- // RS-] = k-1K2[Fe(III)HEDTAOH2][RS-] (14)

[H+]

Substituting equation 14 into equation 11;

Rate = k2k-1K2[Fe(III)HEDTAOH2][RS-] + k4[Fe(III)HEDTAOH2 // RS.] (15)

 [H+]

Also, from equation 8;

[Fe(III)HEDTAOH2 // RS.] = k-3[Fe(III)HEDTAOH2][RS.] (16)

Substituting equation 16 into equation 15;

Rate = k2k-1K2[Fe(III)HEDTAOH2][RS-] + k4k-3[Fe(III)HEDTAOH2][RS.] (17)

 [H+]

If [RSH] = [RS-] = [RS-]2; [RS-] = K11/2[RSH]1/2

Hence,

Rate = k2k-1K2K11/2[Fe(III)HEDTAOH2][RSH]1/2 + k4k-3K11/2[Fe(III)HEDTAOH2][RSH]1/2

 [H+]

 (18)

Rate = (k2k-1K2K11/2[H+]-1 + k4k-3K11/2)[Fe(III)HEDTAOH2][RSH]1/2 (19)

Rate = k[Fe(III)HEDTAOH2][RSH]1/2 (20)

Where k = k2k-1K2K11/2[H+]-1 + k4k-3K11/2

However, equation 20 conforms to experimental rate law.

**4. Conclusion**

The kinetics and mechanism of reduction of N-(2-hydroxyethyl)ethylene- diaminetriacetatoiron(III) complex by thioglycol was studied in bicarbonate buffer medium. A mole ratio of 2:1 (Complex: Oxidant) was obtained. The analysis of other kinetic data obtained under the pseudo-first order condition gave an overall order of one and half; first order with respect to the concentration of the oxidant and half order with respect to the concentration of the reductant Rationalizing the pieces of evidence obtained in the study favors the outer-sphere mechanism and a plausible mechanistic pathway which explains the kinetic data obtained is proposed.

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