KINETICS AND MECHANISMS OF THE REDUCTION OF μ-ADIPATO-DI *(N, N′*BIS (SALICYLIDENE) ETHYLENEDIAMINATOIRON (III) [(Fe-Salen)₂adi] WITH 2-MERCAPTOBENZOTHIAZOLE IN AQUEOUS PERCHLORIC ACID

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ABSTRACT

The kinetics and mechanisms of the reduction of μ-adipato-di*(N,N′*bis(salicylidene) ethylenediaminatoiron (III) [(Fe-salen)₂adi]hereafter denoted as Fe₂adi by 2-mercaptobenzothiazole(BTSH) have been studied spectrophotometrically at 495 nm. At 29 ± 1°C, I= 0.01 mol dm^{-3} (NaClO₄) and [H$^+$] =1.0 x 10^{-3}mol dm^{-3}, the Fe (III) complex was reduced to Fe(II) while the reductant (BTSH) was oxidized to the disulphide (BTSSTB). The results fit the general rate law, $-\dfrac{d[\text{Fe}_2\text{adi}]}{dt}$ = (a+b[H$^+$])[Fe₂adi][Reductant] [H$^+$]

The rate of reaction increased with increase in [H$^+$], decreased with increase in ionic strength of the medium, but were not affected by the decrease in dielectric constant D. Addition of Mg^{2+} and CH₃COO$^-$ ions in small amounts did not affect the rate of reaction of Fe₂adi with BTSH. Michaelis – Menten plot of 1/k$_{obs}$ versus 1/[BTSH] were also linear with intercept for the redox reaction of Fe₂adi with BTSH. The result havsbeen rationalized in terms of plausible inner-sphere mechanism.

Key words: concentration, kinetics, oxidant, reductant, spectrophotometry.

INTRODUCTION

The electron transfer reactions of binuclear iron (III) complexes have attracted a lot of interest in recent time due to their application as models for the investigation of the physiological role played by iron in biochemical processes[2], such as hemerythrin [2,3,4,6] and ferric porphyrin [2,4,5,7].

Very few reports have emerged as regards the mechanisms of their electron transfer reactions. Kinetics and mechanism of the reduction of μ-adipato-di*(N,N′*bis(salicylidene) ethylenediaminatoiron (III) by dithionate ion, S₂O₆$^{2-}$ have been studied at 29°C in aqueous percholoric acid. A 1:1 stoichiometry was determined and the rate of reaction was found to be first order with respect to the complex [Fe₂adi] and zero dependence on [S₂O₆$^{2-}$]. The rate of reaction was observed to increase with increase in [H$^+$], decreased with increased dielectric

constant but was invariant to changes in ionic strength of the medium. The reaction was rationalized on the basis of a proton coupled outer-sphere electron transfer mechanism. [7].In this article, we report an investigation of the dynamics of the electron transfer reaction of μ-adipato - di*(N, N/*bis(salicylidene)ethylenediaminatoiron (III) complex, Fe_2adi with 2-mercaptobenzothiazole (BTSH).The behavior of transition metal ions with respect to their electron transfer and the roles played by bridging ligands in the course of redox reaction formed the bed rock of this study [4,5]. The main advantage of this research is that the results provide additional insight into the complexities attending reactions of bridged iron (III) complexes and the extent of influence of the bridging ligand on the rate of electron transfer. It is therefore hoped that this research will enhance the knowledge of the kinetics and mechanisms of electron transfer reactions of binuclear iron (III) complexes and other transition metal complexes with BTSH.

EXPERIMENTAL

All reagents were of analytical grade and were used without further purification unless otherwise stated. Solution of BTSH was prepared by dissolving it in ethanol. Absorbance of solutions was obtained on Jenway 6305 UV- visible spectrophotometer. Infrared spectra data were obtained on Shimadzu FITR 8400S Fourier transform infrared spectrophotometer.

Synthesis of $\mu-$adipato – di*(N,N/* – bis(salicylidene)ethylenediaminatoiron(III) [(Fe-Salen)₂adi]

The complex was prepared following the literature method [15, 16]. A solution of adipic acid (1.00 mmol) in MeOH (20 mL) was added to a suspension of [(Fe-Salen)₂O] (0.5 g, 0.76 mmol) in MeOH (20 mL). The reaction mixture was well stirred and heated under reflux for 30 minutes where upon it became dark. The solid product was removed by filtration, washed with MeOH and Et_2O and then dried in a desiccator. The complex decomposes between 290-295 ºC. The percentage yield was 43.5%.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [24] . Under the conditions of $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} and ionic strength (I) = 1.0

x 10^{-2}mol dm^{-3} (NaClO$_4$), the concentration of Fe$_2$adi was maintained at 1.0 x 10^{-4}mol dm^{-3} and [BTSH] varied. Plot of absorbance versus [BTSH] / [Fe$_2$adi] were made from which the stoichiometry was evaluated.

Kinetic measurements

All kinetic runs were performed under pesudo-first order conditions with the concentration of BTSH at least 20 fold in excess of [Fe$_2$adi]. The rates of reactions were monitored by following the rate of decrease in the absorbance of Fe$_2$adi at 495nm on Jenway 6305 spectrophotometer. Pseudo – first order rate constant, k_{obs} were obtained from logarithmic plots of absorbance differences against time while second order rate constant, k_2 were determined as k_{obs}/[BTSH]. The reaction was carried out at a temperature of 29 ± 1°C, [H$^+$] = 1.0 x 10^{-3}mol dm^{-3} and I = 1.0 x 10^{-2}mol dm^{-3} (NaClO$_4$) unless otherwise stated.

Test for free radicals

This was carried as follows: Stoichiometric amounts of the oxidant and the reductant solution in excess methanol were mixed with acrylamide as described in the literature [17]. Gel formation in the reaction mixture indicated the presence of free radicals as an important intermediate in this reaction.

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometric studies showed that one mole of Fe$_2$adi were consumed per mole of BTSH oxidized. The result is consistent with equation (i).

Fe$_2$adi + BTSH + H$^+$ $\longrightarrow$ Fe$_2$adiH$_2^+$ + ½ BTSSTB ………………………….. i

Presence of Fe(II) as the product of reaction was confirmed by faint green colour generated on addition of K$_3$Fe(CN)$_6$ to the clear solution of the reaction mixture in the presence of excess reductant when the reaction had gone to completion. This is an indication of possible reduction of one Fe (III) center to Fe (II) while the other Fe (III) center is retained. This result depict that BTSH is one electron reductant in this system. The product of the reaction had an IR spectrum very similar to that of Fe$_2$adi thereby signifying that the adipato bridge in Fe$_2$adi was retained in

the Fe (II) product. This is because the frequency characteristics of Fe-O and Fe –N are still present within the range at 424 cm^{-1} and 659 cm^{-1} for Fe_2adi – BTSH system.

Reaction order

The linearity of the pseudo – first order plots of absorbance difference against time to more than 75% extent of reaction indicates first order dependence of rate of reaction on $[Fe_2adi]$. Also plot of – $logk_{obs}$ versus –log [BTSH] gave a straight line with a slope of 1.46 for BTSH – Fe_2adi system, suggesting that the reaction is first order with respect to [BTSH]. The pseudo – first order rate constant values are shown in Table i.

Table i: Pseudo first order and second order rate constants for the reaction of Fe_2adi and BTSH at $[Fe_2adi] = 1 \times 10^{-4}$ mol dm^{-3}, T = 29 ± 1°C and λ_{max} = 495 nm.

$10^3[BTSH]$ /(mol dm^{-3})	$10^3 [H^+]$ /(mol dm^{-3})	I, 10^2 [$NaClO_4$] / (mol dm^{-3})	$10^4 k_{obs} .s^{-1}$	$10^2 k_2$ / ($dm^3mol^{-1}s^{-1}$)
3.0	1.0	1.0	0.26	0.9
4.0	1.0	1.0	0.43	1.1
5.0	1.0	1.0	0.53	1.1
6.0	1.0	1.0	0.68	1.1
7.0	1.0	1.0	0.86	1.2
5.0	1.0	1.0	0.53	1.1
5.0	5.0	1.0	0.59	1.2
5.0	10.0	1.0	0.71	1.4
5.0	15.0	1.0	0.83	1.7
5.0	20.0	1.0	0.92	1.8
5.0	1.0	1.0	0.53	1.1
5.0	1.0	5.1	0.31	0.6
5.0	1.0	5.5	0.30	0.6
5.0	1.0	6.0	0.29	0.6
5.0	1.0	6.5	0.28	0.6
5.0	1.0	7.0	0.26	0.5

Acid dependence

The effect of change in the concentration of acid $[H^+]$ at constant concentration of Fe_2adi with BTSH was investigated within the range   1.0 x 10 $^{-3}$ mol dm^{-3} ≤ $[H^+]$ ≤ 20.0 x 10^{-3} mol dm^{-3}.

Under these conditions, the rate of reaction increased with increase in $[H^+]$ as shown in table i.A plot of k_{H+} versus $[H^+]$ (figure 1) was linear (r = 0.97) with positive intercept. The dependence of k_{H+} on $[H^+]$ (figure 1) is best fitted into equation ii.

$k_{H+} = (a + b[H^+])$ $[Fe_2adi][BTSH][H^+]$---ii

where a = 0.5×10^{-4} $dm^{-3}mol^{-1}$ s^{-1} and b = 2.0×10^{-3} $dm^6 mol^{-2}s^{-1}$.This rate law is an indication of two parallel pathways for the reaction. The H^+ dependent route is consistent with presence of dissociated BTSH while direct acid dependence suggests protonation the protonation of the Fe(III) complex in acid media.

Effect of ionic strength, dielectric constant and added ions

Changes in the ionic strength of the reaction medium from 1.0×10^{-2} to 7.0×10^{-2} mol dm^{-3} using $NaClO_4$ at $[Fe_2adi] = 1 \times 10^{-4}$ mol dm^{-3}, T = 29 ± 1°C and λ_{max} = 495nm led to the decrease in rate of the reaction, Table i.This negative primary salt effect seems to suggest that the rate determining step involves oppositely charged species.
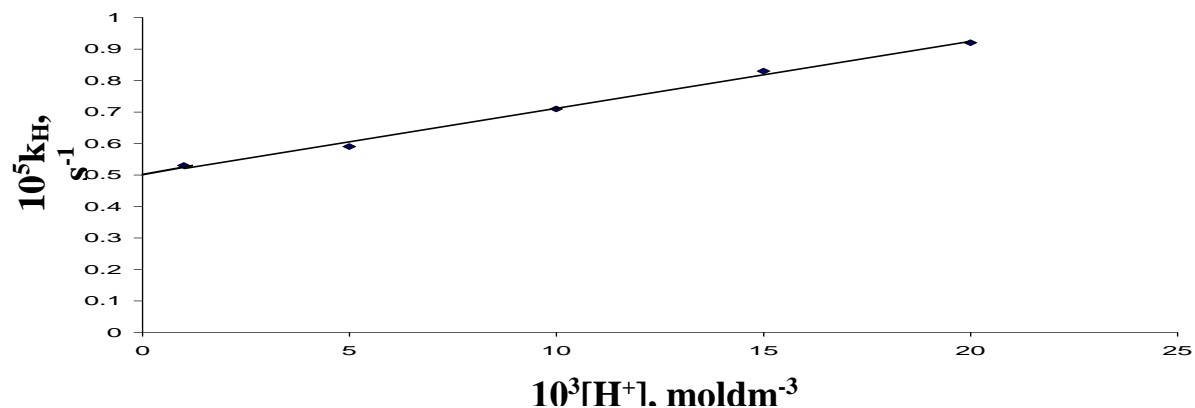

Figure i: Plot of k_H versus $[H^+]$ for the reduction ofFe$_2$adi by BTSH at λ_{max} = 495 nm and T= 29 ± 1°C.

The effect may be attributed to increased shielding of the electrostatic repulsion or attraction of the ions by the ion atmosphere as the concentration of the electrolyte increased. It also showed that reaction occurred most probably between Fe$_2$adi and BTS$^-$ in more than one pathway.
Decreasing the dielectric constant D from 73.22 – 68.28 using (CH$_3$COCH$_3$ / H$_2$O) mixture did not show any remarkable change in the observed rate of reaction (table ii). This result indicates

that the reaction occurred between cation and neutral molecule or free radical at the rate determining step and so involve Fe_2adi and BTSH or BTS^*. The catalytic effect of added cation and anion was investigated by adding various amounts of Mg^{2+} and CH_3COO^- ions in the range $4.0 \times 10^{-3} - 10.0 \times 10^{-3}$ mol dm^{-3}. The results showed that addition of the ions did not affect the rate of reaction of Fe_2adi with BTSH (Table ii). Lack of catalysis observed by the addition of cation and anion may likely be due to the formation of intermediate complex and so is in accordance with inner- sphere mechanism.

Table ii: Dependence of rate constant on added ions, X and on dielectric constant D for the reaction of Fe_2adi with BTSH, at $[Fe_2adi] = 1 \times 10^{-4}$ mol dm^{-3}, $[BTSH] = 0.05$ mol dm^{-3} $[H^+] = 0.05$ mol dm^{-3}, $I = 0.5$ mol dm^{-3} [NaClO$_4$], $\lambda_{max} = 495$ nm, $T = 29 \pm 1$°C.

X	10^3 [X]/(mol dm^{-3})	$10^4 k_{obs}$ / s-1	$10^3 k_2$ /(dm^{3}mol^{-1}s^{-1})
Mg^{2+}	6.0	1.02	2.0
	8.0	1.68	3.4
	10.0	1.82	3.6
	12.0	1.32	2.6
CH_3COO^-	4.0	2.26	4.5
	6.0	1.88	3.8
	8.0	2.11	4.2
	10.0	2.02	4.0
	12.0	1.59	3.2
D73.22		2.30	4.6
71.86		1.84	3.7
70.51		1.67	3.3
69.15		1.76	3.5
68.28		1.85	3.7

Temperature dependence of rate

The rate dependence on temperature for the reaction of Fe_2adi with BTSH was investigated between 10^0C and 30^0C. The rate constant k_{obs} was found to increase from 2.83×10^{-4} to 4.30×10^{-4} as the temperature of the system increases.

From the Erying relation:

$$\log \frac{k_{obs}}{T} = \log \frac{k}{h} + \frac{\Delta S^{\#}}{2.303R} - \frac{\Delta H^{\#}}{2.303RT}$$ --iii

A plot of log k_{obs}/ T versus I / T was constructed and activation parameters were determined. $\Delta H^{\#}$ was derived as 16.47 kJmol^{-1} and $\Delta S^{\#}$ as - 307.12 JK^{-1} mol^{-1}. The relatively large negative value of $\Delta S^{\#}$ suggests that the redox process is spontaneous in the rate determining step. Furthermore, the positive enthalpy of activation corresponds to the activation energy of the reaction where the unstable species of the activated complex dissociate into product under a suitable vibrational frequency. These results give an insight into the stability of the transition state. The same deduction has been made for the reduction of µ-adipato-di (N,N/bis(salicylidene)ethylenediaminatoiron (III) by dithionate [7].

Michaelis- Menten plot

Michaelis - Menten least square fit of 1 / k_{obs} versus 1/ [BTSH] for the reaction of Fe$_2$adi with BTSH gave a straight line with intercept (figure ii). The linearity of the least square fit with outstanding intercept indicates that the intermediate participating in the reaction system have appreciable equilibrium constant. The positive slope of 133.33 mol dm^{-3}s^{-1} signifies that there was no inhibition of reaction as the concentration of thiol (BTSH) increased [23, 24, 25].
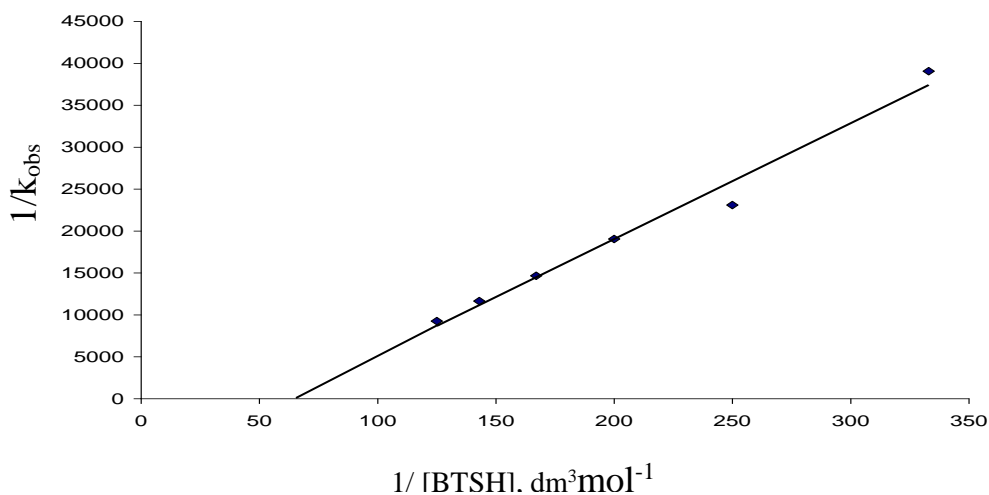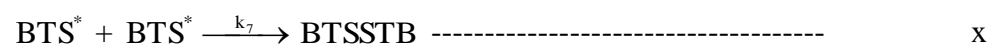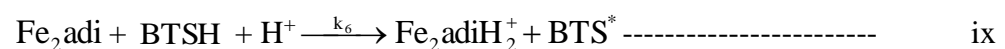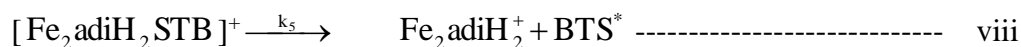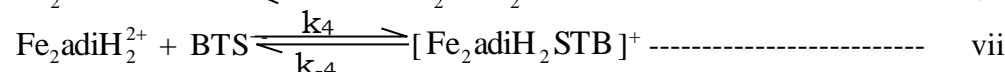

Fig. ii: Michaelis − Menten Plot for the reduction of Fe$_2$adi by BTSH at [Fe$_2$adi] = 1x10^{-4}mol dm^{-3}, [BTSH] = 5X10^{-2}mol dm^{-3}, [H$^+$] = 1X10^{-3}mol dm^{-3}, I = 1X10^{-2}mol dm^{-3} NaClO$_4$] and λ_{max} = 495 nm.

Reaction Mechanism

Based on the stoichiometry and the kinetic results, the following mechanism was proposed for the reaction between Fe_2adi and BTSH.

$$Fe_2adi + H^+ \xrightarrow{K_1} Fe_2adiH^+ \quad \text{---} \qquad \text{iv}$$

$$BTSH \xrightarrow{K_2} BTS^- + H^+ \quad \text{--} \qquad \text{v}$$

$$Fe_2adiH^+ + H^+ \underset{}{\overset{k_3}{\rightleftharpoons}} Fe_2adiH_2^{2+} \quad \text{---------------------------------} \qquad \text{vi}$$

$$Fe_2adiH_2^{2+} + BTS \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Fe_2adiH_2STB]^+ \quad \text{-------------------------} \qquad \text{vii}$$

$$[Fe_2adiH_2STB]^+ \xrightarrow{k_5} Fe_2adiH_2^+ + BTS^* \quad \text{----------------------------} \qquad \text{viii}$$

$$Fe_2adi + BTSH + H^+ \xrightarrow{k_6} Fe_2adiH_2^+ + BTS^* \quad \text{------------------------} \qquad \text{ix}$$

$$BTS^* + BTS^* \xrightarrow{k_7} BTSSTB \quad \text{-------------------------------------} \qquad \text{x}$$

$$\text{Rate} = k_5[Fe_2adiH_2STB]^+ + k_6[Fe_2adi][BTSH][H^+] \quad \text{----------------} \qquad \text{xi}$$
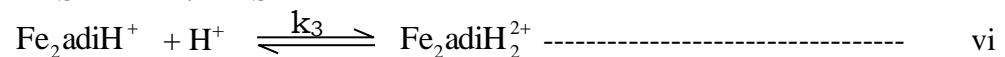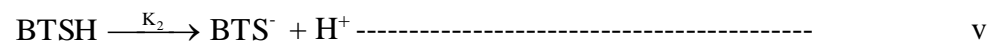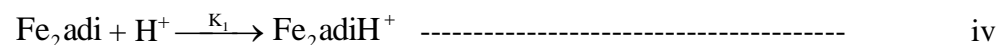
By applying steady state approximation.

$$\frac{-d[Fe_2adiH_2STB]^+}{dt} = k_4[Fe_2adiH_2^{2+}][BTS^-] - k_{-4}[Fe_2adiH_2STB]^+ - k_5[Fe_2adiH_2STB]^+ = 0$$

$$k_4[Fe_2adiH_2^{2+}][BTS^-] = k_{-4}[Fe_2adiH_2STB]^+ + k_5[Fe_2adiH_2STB]^+$$

$$[Fe_2adiH_2STB]^+ = \frac{k_4[Fe_2adiH_2^{2+}][BTS^-]}{k_{-4} + k_5}$$

If $k_{-4} \ll k_5$, then $[Fe_2adiH_2STB]^+ = \dfrac{k_4[Fe_2adiH_2^{2+}][BTS^-]}{Fe_2adiH_2^{2+}k_5}$ ------------ xii

From equation vi, $= k_3[Fe_2adiH^+][H^+]$ --------------------------xiii

Also from equation iv $[Fe_2adiH^+] = K_1[Fe_2adi][H^+]$ ----------------------- xiv

Putting equation xiv into equation.xiii gives,

$$[Fe_2adiH_2^{2+}] = K_1k_3[Fe_2adi][H^+]^2 \quad \text{--------------------------------------} \qquad \text{xv}$$

From equation v, $[BTS^-] = K_2[BTSH]$ -- xvi

Putting equations xv and xvi into equation xii gives

$$[Fe_2adiH_2STB]^+ = \frac{K_1K_2k_3k_4[Fe_2adi][H^+]^2[BTSH]}{k_5} \quad \text{----------------} \text{xvii}$$

Substituting equation xviiinto equation xi gives

$$\text{Rate} = \frac{K_1 K_2 k_3 k_4 k_5 [\text{Fe}_2 adi][H^+]^2 [BTSH]}{k_5} + k_6 [\text{Fe}_2 adi][BTSH][H^+]$$

$$= K_1 K_2 k_3 k_4 [\text{Fe}_2 adi][BTSH][H^+]^2 + k_6 [\text{Fe}_2 adi][BTSH][H^+]$$

$$= \left(k_6 + K_1 K_2 k_3 k_4 [H^+] \right) [\text{Fe}_2 adi][BTSH][H^+] \quad \text{------------------------------xviii}$$

Equation xviii is similar to equation ii where

$a = k_6 = 5.0 \times 10^{-5} dm^3 mol^- s^{-1}$ and $b = K_1 K_2 k_3 k_4 = 2.0 \times 10^{-3} dm^6 mol^{-2} s^{-1}$

With regard to the above mechanism the system can be said to follow the inner – sphere electron transfer pathway. This is due to the fact that, since the complex is coordinatively unsaturated, the ease of formation of a ligan-bridged intermediate of inner sphere character is prominent. This reasoning is supported by (a) the presence of spectrophotometric evidence for the formation of precursor complex on scanning the reaction which shows a shift in λ_{max}. (b) theMichaelis – Menten plot of $1/k_{obs}$ versus $1/[BTSH]$ for the reaction of Fe₂adi with BTSH was linear with appreciable intercept thereby signifying the presence of stable intermediate with equilibrium constant. These facts support the inner – sphere redox pathway for the system.

CONCLUSION

The possibility of reducing Fe(III) complex to Fe(II)using(BTSH) has been demonstrated. This suggests the use of 2-mercaptobenzothiazole in detoxification of heavy metals. On the other hand, the oxidation of BTSH which is a toxic pollutant to the disulphide BTSSTB by Fe(III)reduces itsits toxicity.

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