

KINETICS AND MECHANISM OF THE OXIDATION OF THIOSULPHATE ION BY TETRAKIS (2,2'-BIPYRIDINE)- μ -OXODIIRON (III) ION IN AQUEOUS ACIDIC MEDIUM

S.O. IDRIS⁺, J.F. IYUN and E.B. AGBAJI

Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

(Received: January 2007; Accepted: February 2008)

Abstract

The kinetics of the oxidation of thiosulphate ion by tetrakis(2,2'-bipyridine)- μ -oxodiiron(III) ion has been investigated in aqueous acidic medium at 30°C. Increase in concentration of acid increased the reaction rate. The reaction obeyed a general rate law:

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

where $k_{obs} = a + b [H^+]^2$

Added anions have no effect on the reaction rate. The outersphere mechanistic pathway is proposed for the reaction.

Key words: Kinetics, reduction, mechanism, oxobridged binuclear complex ion, outer-sphere

1. Introduction

The study of oxobridged binuclear complexes of iron is important as information obtained may go a long way in helping to interpret some of the observed behaviours of metalloenzymes. Various complexes of this nature have been synthesized and characterized (Cohen, 1969; Gaines, *et al.*, 1936; Khedekar *et al.*, 1967; Schugar *et al.*, 1967, 1969, 1972; Reiff *et al.*, 1968; Reiff, 1971; David *et al.*, 1972; David, 1973). Also other reports on these complexes focused on their stabilities in acid and aqueous media (Baesi and Mesner, 1976; David and de Mello, 1973) but literature on their electron transfer reaction is scanty. We therefore, carried out kinetic investigation on the electron transfer reaction of tetrakis (2,2'-bipyridine)- μ -oxodiiron (III) ion hereafter referred to as Fe_2O^{4+} and $S_2O_3^{2-}$, to gain more insight into the redox pattern of these species.

2. Experimental

Tetrakis(2,2'-bipyridine)- μ -oxodiiron (III) chloride, $[Fe_2(bipy)_4O]Cl_4$ was prepared, purified and characterized as described by David (1973). The complex was not stable in acid concentration greater than 10^{-4} mol dm⁻³. Hence kinetic studies were limited to 1×10^{-6} mol dm⁻³ $\leq [H^+] \leq 120 \times 10^{-6}$ mol dm⁻³. Fresh

standard solutions of this complex and $Na_2S_2O_3$ were prepared prior to stoichiometric and kinetic studies. HCl (M&B) was used to investigate effect of $[H^+]$ on the reaction rate. NaCl (Analar) was employed as the inert electrolyte for maintaining a constant ionic strength (I) for each run. All reagents used were of analytical grade except otherwise stated.

Stoichiometry

The stoichiometry of this reaction was determined by spectrophotometric titration. The absorbance of solutions containing various concentrations of $S_2O_3^{2-}$ in the range 1×10^{-5} to 32×10^{-5} mol dm⁻³ and a constant $[Fe_2O^{4+}]$ of 8×10^{-5} mol dm⁻³ at ionic strength, $I = 0.01$ mol dm⁻³, $[H^+] = 5 \times 10^{-5}$ mol dm⁻³ and $T = 30$ °C, were measured at 520 nm after the reaction had gone to completion. The stoichiometry was subsequently evaluated from the plot of absorbance versus $[S_2O_3^{2-}]$ (Fig.1).

Kinetic studies

The rate of the reaction was monitored by measuring the rate of increase in absorbance of the product at its λ_{max} (520 nm) after having certified that none of the reactants had any significant absorbance at this wavelength using Chroma 254 Digital Colorimeter. All kinetic runs were carried out under pseudo-first

+ corresponding author (email: alhajisoidris@yahoo.com)

order condition with the [reductant] in at least 200-fold excess over that of the oxidant. The ionic strength was maintained at 0.2 mol dm^{-3} and $[\text{H}^+] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ and $T = 30 \text{ }^\circ\text{C}$ except otherwise stated.

Test for free radicals

Test for the polymerization of allylacetate, a known sulphate ion radical scavenger by partly reaction moisture in excess methanol was carried out as described earlier (Lawal, 1997).

Effect of dielectric constant (D) on the reaction rate

This was done by following the procedure described earlier (Ukoha and Iyun, 2001).

Product analysis

SO_4^{2-} was qualitatively identified by the addition of BaCl_2 solution and excess dilute HCl to the oxidized mixture while Fe^{2+} was identified spectroscopically.

3. Results and Discussion

Stoichiometric investigation indicated that one mole of $\text{S}_2\text{O}_3^{2-}$ is oxidized per mole of Fe_2O^{4+} reduced as shown in equation (1)



Formation of white precipitate on addition of BaCl_2 solution to the product solution which remained insoluble on addition of excess dilute HCl indicated the presence of SO_4^{2-} as one of the reaction products. The appearance of an absorption maximum at 520 nm also confirmed the formation of Fe^{2+} (Ayoko *et al.*, 1993; Iyun *et al.*, 1996; Iyun, 2004; Idris *et al.*, 2004, 2005). Also the absence of absorption peak at 620nm in the product solution negated the presence of mononuclear Fe^{3+} in the reaction medium (Iyun *et al.*, 1996).

Pseudo-first order plot of $\log(A_\infty - A_t)$ against time were linear to about 40% extent of reaction. The observed rate constants (k_{obs}) were therefore determined from the initial point of the reaction. Literature has shown that result of this nature is reminiscent of product inhibition during the course of the reaction (Iyun, 2004). The values of the observed first order rate constant for this reaction are independent of $[\text{S}_2\text{O}_3^{2-}]$ (Table 1), an indication that the reaction is zero order in [reductant], hence first order overall. At 520nm, the rate equation can be represented by equation (2)

$$\frac{1}{2} \frac{d[\text{Fe}^{2+}]}{dt} = k_{\text{obs}}[\text{Fe}_2\text{O}^{4+}] \quad (2)$$

Earlier reports have indicated that overall order of one as in the titled reaction was observed in the reactions of another oxyanion of sulphur, $\text{S}_2\text{O}_5^{2-}$ with triphenylmethane dye (Onu and Iyun, 2001) and basic fuchsin (Lawal, 1997).

In the acid range 10×10^{-6} to $120 \times 10^{-6} \text{ mol dm}^{-3}$, k_{obs} was found to increase as $[\text{H}^+]$ increase (Table 1). A plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ was linear with in an intercept, and can be represented by the relationship:

$$k_{\text{obs}} = a + b [\text{H}^+]^2 \quad (3)$$

Increase in rate of reaction with increase in $[\text{H}^+]$ is a common feature of redox reactions involving oxyanions (Idris *et al.*, 2004, 2005)

Variation of ionic strength of the reaction medium in the range $0.10 \text{ mol dm}^{-3} \leq I \leq 0.30 \text{ mol dm}^{-3}$ using NaCl did not have any influence on the reaction rate (Table 2). This observation is a common characteristics of reaction occurring between ion and neutral molecule where the product of the charges is zero at the transition state (Atkins and de Paula, 2002). This rationalization is also supported by the fact that changes in dielectric constant (D) of the reaction medium had no effect on reaction rate (Table 2). The reduction in k_{obs} as D decreased from 81 to 80.2 could be due to interaction between propan-2-one and the redox partners as further reduction of D did not have any effect on k_{obs} .

Test for polymerization of allylacetate was positive, an indication that participation of free radicals is important in this reaction. Similar result was obtained in the reaction of $\text{S}_2\text{O}_3^{2-}$ and $\text{M}_n^{\text{III}}\text{O}_2\text{M}_n^{\text{IV}}$ (Babatunde and Iyun, 2004).

Addition of varying concentration of ClO_4^- and NO_3^- did not influence the rate of the titled reaction (Table 2). This may suggest that the reaction proceeded by the innersphere mechanistic pathway (Przystas and Sutin, 1973; Adegite *et al.*, 1977). However, spectroscopic studies of the reaction mixture did not implicate stable intermediate complex as there was no shift in λ_{max} on scanning the reaction mixture.

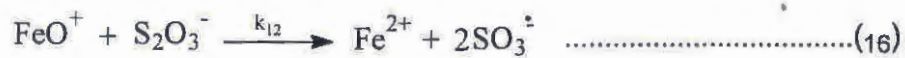
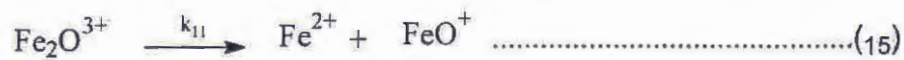
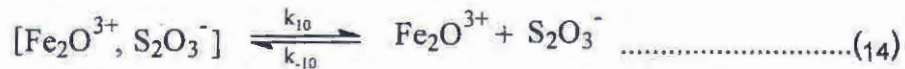
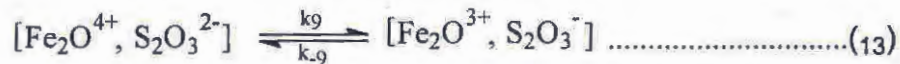
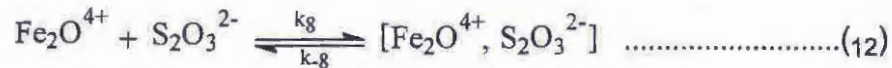
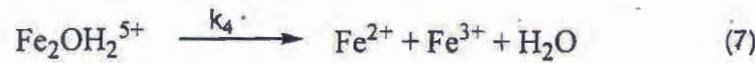
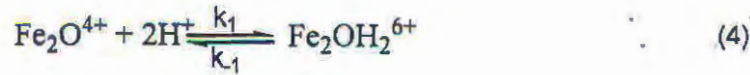
Taking recourse to the experimental data, it is a apparent that dissolved oxygen in the reaction medium participated actively in the redox process of this reaction. Hence the scheme below is proposed to explain these observations.

Table 1: Pseudo-first order rate constant for the reaction of Fe_2O^{4+} and $\text{S}_2\text{O}_3^{2-}$ at $[\text{Fe}_2\text{O}^{4+}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 520 \text{ nm}$ and $T = 30^\circ\text{C}$

$10^3[\text{S}_2\text{O}_3^{2-}], \text{mol dm}^{-3}$	$10^6[\text{H}^+], \text{mol dm}^{-3}$	$10^2 I, \text{mol dm}^{-3}$	$10^3 k_{\text{obs}}, \text{s}^{-1}$
20	50	20	3.88
23	50	20	3.74
25	50	20	3.83
27	50	20	4.09
30	50	20	3.95
25	10	20	3.66
25	20	20	4.13
25	40	20	4.73
25	80	20	7.68
25	120	20	9.40
25	50	10	4.14
25	50	15	3.92
25	50	20	4.09
25	50	25	4.02
25	50	30	3.64

Table 2: Dependence of rate constant on anions (X) and on dielectric constant (D) of the reaction medium for the reaction of Fe_2O^{4+} and $\text{S}_2\text{O}_3^{2-}$ at $[\text{Fe}_2\text{O}^{4+}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_3^{2-}] = 25 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 520 \text{ nm}$ and $T = 30^\circ\text{C}$

X	$10^4[\text{X}], \text{mol dm}^{-3}$	$10 k_{\text{obs}}, \text{s}^{-1}$
NO_3^-	40	4.16
	80	4.16
	100	4.09
	140	4.02
	180	4.06
ClO_4^-	1	3.93
	40	3.88
	80	4.02
	100	3.88
	140	4.01
	180	3.88
D		
	81	4.02
	80.2	2.44
	78.6	2.43
	77	2.71
	75.8	2.71
	74.6	2.65



$$\text{Rate} = k_4 [\text{Fe}_2\text{OH}_2^{5+}] + k_{11} [\text{Fe}_2\text{O}^{3+}] \quad \dots\dots\dots(18)$$

When steady state hypothesis is applied to the acid dependent path,

$$[\text{Fe}_2\text{OH}_2^{5+}] = \frac{k_3 [\text{Fe}_2\text{OH}_2^{6+}, \text{S}_2\text{O}_3^{2-}]}{k_{-3} [\text{S}_2\text{O}_3^-]} \quad \dots\dots\dots(19)$$

The rate of acid dependent path then becomes:

$$\text{Rate} = \frac{k_4 k_3 [\text{Fe}_2\text{OH}_2^{6+}, \text{S}_2\text{O}_3^{2-}]}{k_{-3} [\text{S}_2\text{O}_3^-]} \quad \dots\dots\dots(20)$$

But $[Fe_2OH_2^{6+}, S_2O_3^{2-}] = K_2K_1 [Fe_2O^{4+}][H^+]^2[S_2O_3^{2-}] \dots\dots (21)$

Hence equation (20) becomes :

$$\text{Rate} = \frac{K_1K_2k_3k_4[Fe_2O^{4+}][H^+]^2[S_2O_3^{2-}]}{k_{-3}[S_2O_3^-]} \dots\dots\dots (22)$$

If $[S_2O_3^{2-}] \approx k_3[S_2O_3^-]$, equation (22) reduces to

$$\text{Rate} = K_1K_2k_3k_4 [Fe_2O^{4+}][H^+]^2 \dots\dots\dots(23)$$

In addition, application of similar treatments to acid independent path leads to the expression:

$$\text{Rate} = \frac{K_8k_9k_{11}k_{10}}{k_{-9} + k_{10}} [Fe_2O^{4+}] \dots\dots\dots(24)$$

Therefore, overall reaction rate = $\frac{K_8k_9k_{11}k_{10}}{k_{-9} + k_{10}} [Fe_2O^{4+}] + K_1K_2k_3k_4[H^+]^2 [Fe_2O^{4+}]$

$$= \left(\frac{K_8k_9k_{11}k_{10}}{k_{-9} + k_{10}} + K_1K_2k_3k_4[H^+]^2 \right) [Fe_2O^{4+}] \dots\dots\dots(25)$$

Equation (25) is similar to equation (2) where: $\left(\frac{K_8k_9k_{11}k_{10}}{k_{-9} + k_{10}} + K_1K_2k_3k_4[H^+]^2 \right) = k_{obs}$

It seems reasonable to surmise from the substitution inertness of Fe_2O^{4+} and the steric hindrance expected from its bulky nature that the outersphere mechanism is much more favoured in this reaction than the innersphere. When these arguments are considered alongside the absence of spectroscopic and kinetic evidence of intermediate complex formation, the plausibility of innersphere mechanism is remote. Therefore, the outersphere mechanism is proposed for this reaction.

Acknowledgement

We are grateful to Ahmadu Bello University for the award of research grant to S.O Idris to carryout this study.

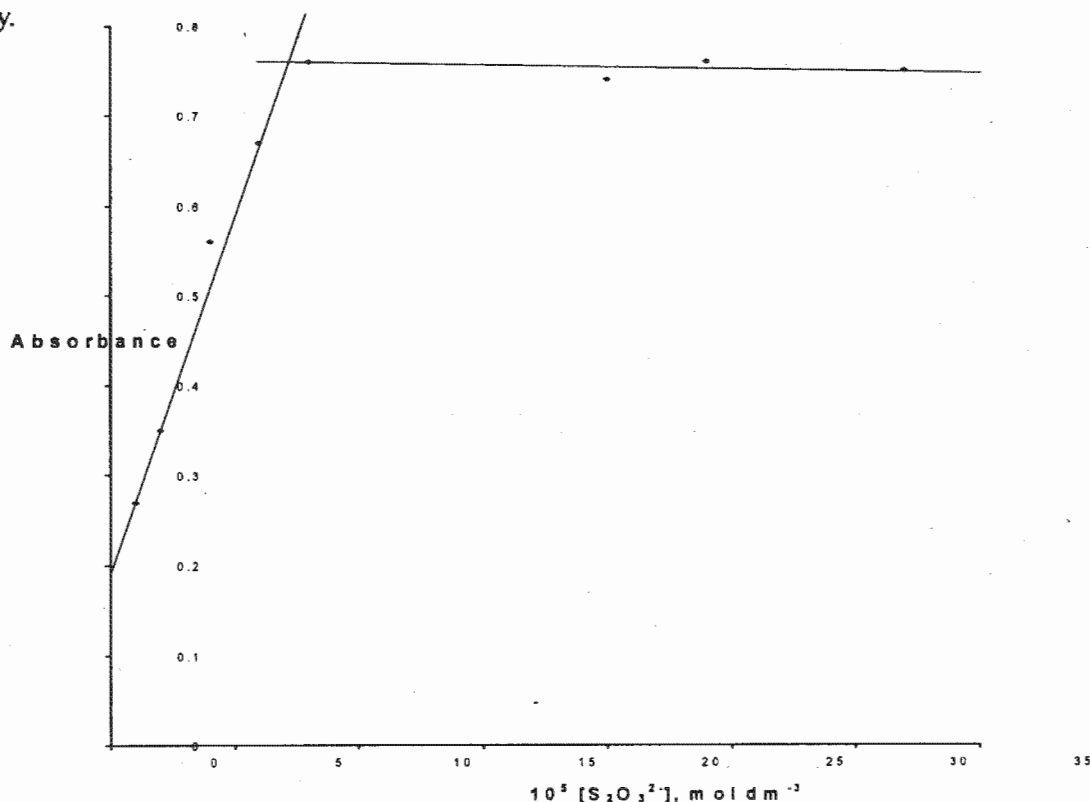


Fig. 1: Stoichiometry of the reduction of Fe_2O^{4+} by $S_2O_3^{2-}$

REFERENCES

- Adegite, A., Iyun, J.F. and Ojo, J.F., 1977. Kinetics and mechanisms of electron transfer reactions between uranium (III) and some ruthenium(III)ammine complexes. *J. Chem. Soc. Dalton*, 115.
- Atkins, P. and de Paula, J., 2002 *Physical Chemistry*. 7th ed. Oxford University Press, 962.
- Ayoko, G.A., Iyun, J.F. and Mamman, S., 1993. Oxidation of N-(2-hydroxyethyl) ethylenediamminetriacetate by trispoly(pyridyl) iron (III) complexes and the dodecatungstocobaltate(III) ion. *Transition Met. Chem.*, 18, 475 – 477.
- Babatunde, O.A. and Iyun, J.F., 2004. Kinetics of the reduction of di- μ - oxo-tetrakis (1, 10 - phenanthroline) – dimanganese (III, IV) perchlorate by thiosulphate ions in-acid medium. *ChemClass Journal*, 1-5.
- Baesi, C.F. and Mesner, R.E., 1976. *The hydrolysis of cations*. John Wiley and Sons, New York, 232 – 234.
- Cohen, I.A., 1969. The dimeric nature of hemin hydroxides, *J. Am. Chem. Soc.*, 91, 1980.
- David, P.G., 1973. Binuclear and Mononuclear mixed ligand complexes of iron (III) with thiocyanate and aromatic diimines. *J. Inorg. Nucl. Chem.*, 35, 1463-1470.
- David, P.G. and de Mello, P.C., 1972. Kinetics of the dissociation of binuclear oxygen – bridged complexes of iron (III) with 1,10 – phenanthroline and 2,2' – bipyridine . *Inorg. Chem.*, 12 (9), 2188–2192.
- David, P.G., Richardson, J.G. and Wehry, E.L., 1972. Photoreduction of tetrakis (1,10 - phenanthroline) - μ - oxodiiron(III) complexes in aqueous and acetonitrile solution. *J. Inorg. Nucl. Chem.*, 1333–1346.
- Gaines (Jnr), A., Hammett, L.P. and Walden, G.H., 1936. The structure and properties of mononuclear and polynuclear phenanthroline – ferric complexes. *J. Am. Chem. Soc.*, 58, 1688.
- Idris, S.O., Iyun, J.F. and Agbaji, E.B., 2004. Kinetics and Mechanism of the oxidation of catachol by $\text{Fe}_2(\text{bipy})_4\text{O}^{4+}$ in aqueous hydrochloric acid medium. *ChemClass Journal*, 27-30.
- Idris, S.O., Iyun, J.F. and Agbaji, E.B., 2005. The mechanism of electron transfer reaction of $[\text{Fe}_2(\text{bpy})_4\text{O}]\text{Cl}_4$ with metabisulphite ions in aqueous acidic medium. *ChemClass Journal*, 85-87.
- Iyun, J.F., 2004. The oxidation of some tris (diimine) iron (II) and tris (substituted diimine) Iron (II) complexes by aqueous acidic bromine solution. An assessment of the marcus model for non – complimentary reactions. *ChemClass Journal*. 59-63.
- Iyun J. F., Faruk, U. and Ayoko, G. A., 1996. Reduction of tris (1, 10- phenanthroline) iron (III) ions by arsenious acid. *International Journal of BioChemiPhysics*, 5(1 & 2), 25-28.
- Khedekar, A.V., Lewis, J., Mabbs, F.E. and Weigold, H., 1967. The composition and magnetic properties of some iron (III) 1, 10-phenanthroline and bipyridyl complexes. *J. Chem. Soc. (A)*, 1561-1564.
- Lawal H. M., 1997. *The electron transfer reactions of pararosaniline chloride (Basic fuchsin) and trisoxalatocobaltate (III) iron in acidic medium*. Ph.D Thesis, Abubakar Tafawa Balewa University, Bauchi Nigeria.
- Onu, A. D. and Iyun, J.F., 2001. Triphenylmethane dye redox kinetics: Metabisulphite reduction of rosaniline monochloride. *J. Chem. Soc. Nigeria*, 26(2), 156-159.
- Przystas, T.J. and Sutin, N., 1973 Kinetic studies of anion assisted outer-sphere electron transfer reactions. *J. Am. Chem. Soc.*, 95, 5545.
- Reiff, W.M., 1971. Strongly coupled, oxo-bridged iron (III) complexes magnetically perturbed Mossbauer spectra. *J. Chem. Phys.*, 54 (11), 4718 – 4722.
- Reiff, W.M., Baker (Jr), W. A. and Erickson, N.E., 1968. Studies of some binuclear, oxygen – bridged complexes of iron (III). New iron (III) -2, 2', 2'' –terpyridine complexes. *J. Am. Chem. Soc.*, 90, 4794 – 4800.
- Schugar, H., Walling, C., Jones, R. B. and Gray, H .B., 1967. The structure of iron (III) in aqueous solution. *J. Am. Chem. Soc.*, 89, 3712-3714.
- Schugar, H.J., Hubbard, A.T., Anson, F.C and Gray, H.B., 1969. Electronical and Spectral studies of dimeric iron (III) complexes. *J. Am. Chem. Soc.*, 91, 71-73.
- Schugar, H.J., Rossman, G.R., Barraclough, C.G and Gray, H.B., 1972. Electronic structure of oxo-bridged iron (III) dimers. *J. Am. Chem. Soc.*, 94, 2683-2685.
- Ukoha, P.O. and Iyun, J.F., 2001. Kinetics of reduction of an iron (III) complex ion by mercaptoethanol and mercaptoethylamine in perchloric acid medium. *J. Chem. Soc., Nigeria*, 26(2), 163-163.