

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

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ABSTRACT

The stoichiometry and kinetics of oxidation of metabisulphite ions by $[\text{Fe}_2(\text{bpy})_4\text{O}]\text{Cl}_4$ have been studied spectrophotometrically at $\lambda_{\text{max}} = 520 \text{ nm}$ and $T = 30 \pm 0.5^\circ\text{C}$. The reaction is consistent with the general rate law:

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

The rate of the reaction was unaffected by added anions and change in ionic strength of the reaction medium. The reaction has been rationalized in terms of plausible outer-sphere mechanistic pathway via ion-pair intermediate.

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INTRODUCTION

There has been a great deal of interest in the chemistry of oxo-bridged complexes of Fe^{3+} [1-6]. This most probably stems from the fact that structures of these complexes are closely related to biological systems such as the protein hemerythrin and ferriporphyrins [7-10].

In our earlier studies, we reported the kinetics of reduction of these complexes with mercaptoethylamine and mercaptoethanol [9], L-ascorbic acid [10] and 1,2-benzenediol [11]. The results of these investigations suggest that anion catalysis may or may not be important and also participation of pre-electron transfer binuclear intermediate prior to rate determining step has not been identified during the course of these reactions. This paper is the result of our continuing interest in probing the reactivity of the relatively uninvestigated $[\text{Fe}_2(\text{bpy})_4\text{O}]\text{Cl}_4$. Our hope is that the results might provide the much needed information relating to the reduction of the iron complexes in biological systems.

EXPERIMENTAL

Materials

All the reagents used were of analytical grades and were used as supplied. Oxo-bridged binuclear complex, $[\text{Fe}_2(\text{bpy})_4\text{O}]\text{Cl}_4$ hereafter represented by Fe_2O^{4+} was prepared, purified and characterized as described in the literature [5]. This complex was unstable in the acid concentration greater than 10^{-4} mol

dm^{-3} hence the kinetic studies were limited to $1 \times 10^{-6} \text{ mol dm}^{-3} \leq [\text{H}^+] \leq 120 \times 10^{-6} \text{ mol dm}^{-3}$. Standard solutions of this complex and sodium metabisulphite were prepared freshly prior to kinetic and stoichiometric studies and were kept in the dark because of possible photochemical decomposition.

Effects of $[\text{H}^+]$, added anions and ionic strength of the reaction medium on reaction rate

NaCl was used to maintain the ionic strength of the reaction constant while HCl was used to investigate the effect of $[\text{H}^+]$ on the reaction after it has been standardized titrimetrically. NaNO_3 and NaClO_4 were used to probe the effect of anions on the reaction rate.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions containing known concentration of Fe_2O^{4+} ($1 \times 10^{-5} \text{ mol dm}^{-3}$) and varying concentration of $\text{S}_2\text{O}_5^{2-}$ ($4 \times 10^{-5} \text{ mol dm}^{-3} - 36 \times 10^{-5} \text{ mol dm}^{-3}$) were reacted at $[\text{H}^+] = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.01 \text{ mol dm}^{-3}$, $T = 30^\circ\text{C}$ and $\lambda_{\text{max}} = 520 \text{ nm}$.

Kinetics studies

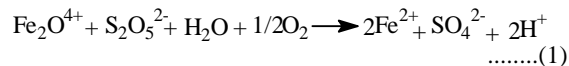
The rate of the reaction was monitored by measuring the increase in absorbance of the product at its λ_{max} (520 nm), after having certified that none of the reactants had any significant absorbance at this wavelength using Chroma 254 Digital Colorimeter. All kinetic measurements were carried out under

pseudo-first order conditions with the $[S_2O_5^{2-}]$ in at least 120 fold excess over that of $[Fe_2O^{4+}]$.

Product analysis

The inorganic product of the reaction was identified qualitatively by the addition of $BaCl_2$ and dilute HCl to the oxidized mixture.

RESULTS AND DISCUSSION



The result of the stoichiometric studies showed that one mole of the oxidant was consumed per mole of $S_2O_5^{2-}$ oxidized according to equation (1) SO_4^{2-} was identified qualitatively by formation of white precipitate on addition of dilute HCl and $BaCl_2$ solutions to the reaction product. The product of the reduction of the complex under kinetic conditions was confirmed to be Fe(II) by the spectral characteristics [12-15] of the product solution.

The linearity of the pseudo-first order plots to over 80% extent of reaction indicates first order dependence on the oxidant. The observed rate constants (k_{obs}) were evaluated from the slope of the initial rates of the reaction. The invariance of k_{obs} with $[S_2O_5^{2-}]$ over the range indicated in Table 1 shows zero order dependence on the reductant. The experimental rate law for this reaction can therefore be written according to equation (2).

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

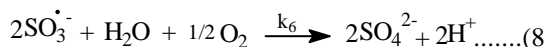
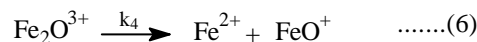
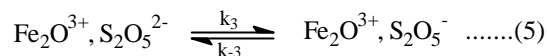
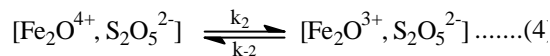
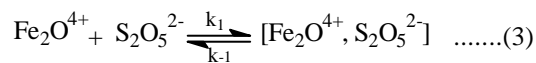
The observed rate constants was determined at various $[H^+]$ at constant [reactants] and ionic strength of the reaction medium (Table 1). The rate of the reactions was found to be independent of $[H^+]$. This result is consistent with our earlier finding reported for the reduction of this oxidant by 1,2- benzenediol [11].

Variation of ionic strength of the reaction medium using NaCl did not affect the rate of the reaction (Table 1). Although this observation is a common feature of reaction occurring between ion and neutral species where the product of the charges is zero at the transition state [16], the transition state as proposed in this reaction involves only intermediate product of the oxidant. Hence changes in ionic strength of the reaction medium and added anions did not alter the reaction rate (Table 1 and 2).

Addition of allylacetate, an effective sulphate radical scavenger in excess methanol to a partially oxidized mixture resulted in the formation of

precipitate. This is an indication of participation of free radicals in the reaction.

On the basis of the above findings, the following



mechanism is proposed as the mechanistic steps for the title reaction.

$$Rate = k_4 [Fe_2O^{3+}] \quad \dots\dots(9)$$

According to steady state hypothesis,

$$[Fe_2O^{3+}] = \frac{k_4 k_3 [Fe_2O^{3+}, S_2O_5^-]}{k_{-3} [S_2O_5^-]} \quad \dots\dots(10)$$

Substitution of equation (10) into (9) leads to

$$Rate = \frac{k_4 k_3 [Fe_2O^{3+}, S_2O_5^-]}{k_{-3} [S_2O_5^-]} \quad \dots\dots(11)$$

Also

$$[Fe_2O^{3+}, S_2O_5^-] = \frac{k_2 [Fe_2O^{4+}, S_2O_5^{2-}]}{k_{-3} + k_{-2}} \quad \dots\dots(12)$$

Substitution of equation (12) into (11) leads to

$$Rate = \frac{k_2 k_3 k_4 [Fe_2O^{4+}] [S_2O_5^{2-}]}{(k_{-3} + k_{-2})(k_{-3} [S_2O_5^-])} \quad \dots\dots(14)$$

If $[S_2O_5^{2-}] \approx k_3 [S_2O_5^-]$, equation (14) reduces to

$$Rate = \frac{k_2 k_3 k_4 [Fe_2O^{4+}]}{k_{-3} + k_{-2}} \quad \dots\dots(15)$$

Equation (15) is similar to equation (2) Where

$$\frac{k_2 k_3 k_4}{k_{-3} + k_{-2}} = k_{obs} \quad \dots\dots(16)$$

It seems reasonable to surmise from the steric hindrance expected from the bulky substrate that outer-sphere mechanism is much more favored in this reaction. When this argument is considered alongside the absence of spectroscopic and kinetic evidence for intermediate complex formation, it appears that the possibility of the inner-sphere mechanistic pathway is remote. These views are reinforced by the absence of anions catalysis which might be due to the fact that rate

determining step in this reaction involves only the intermediate product of the oxidant (equation 6). This species is very unlikely to exhibit any interaction with the added anions, hence the observed trend of anion effect on the reaction rate. Therefore, outer-sphere pathway via the ion-pair intermediate is proposed for this reaction.

Table 1: Pseudo – first order rate constant for the reaction of Fe_2O^{4+} and $S_2O_5^{2-}$ at $[Fe_2O^{4+}] = 3.33 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 520 \text{ nm}$ and $T = 30 \pm 0.5^\circ\text{C}$

$10^4[S_2O_5^{2-}]$, mol dm^{-3}	$10^6[H^+]$, mol dm^{-3}	$10^2 I$, mol dm^{-3}	$10^3 k_{\text{obs}}$, s^{-1}
40.0	60	10	41
43.3	60	10	40
50.0	60	10	43
70.0	60	10	38
50	1	10	42
50	60	10	42
50	80	10	41
50	100	10	41
50	120	10	43
50	60	2	39
50	60	10	44
50	60	15	42
50	60	15	42
50	60	20	42

Table 2: Dependence of rate constant on anions for the reaction of Fe_2O^{4+} and $S_2O_5^{2-}$ at $[Fe_2O^{4+}] = 3.33 \times 10^{-5} \text{ mol dm}^{-3}$, $[S_2O_5^{2-}] = 50 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 6 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 520 \text{ nm}$ and $T = 30 \pm 0.5^\circ\text{C}$

X	$10^4[X]$, mol dm^{-3}	$10 k_{\text{obs}}$, s^{-1}
NO_3^-	1	38
	20	41
	40	39
	80	39
	100	41
ClO_4^-	40	40
	60	40
	80	40
	140	42

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