

The Influence of Ag^+ Ions on the Kinetics of Oxidation of $\text{Fe}(\text{phen})_3^{2+}$ by Peroxodisulphate in Neutral Aqueous Solution

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The influence of Ag^+ ions on the kinetics of ferroin oxidation by peroxodisulphate in a neutral medium has been investigated. It was found that the oxidation proceeds by two parallel pathways—the catalyzed one and non-catalyzed one. The rate constants of both processes were determined and a reaction mechanism has been proposed.

Introduction

The reaction of $\text{Fe}(\text{phen})_3^{2+}$ with peroxodisulphate, in contrast to that with $\text{Ce}(\text{IV})$ [1, 2], proceeds rather slowly. The oxidation of the ferroin, 5-methylferroin, and of the $\text{Fe}(\text{II})$ complexes with 2,2'-bipyridyl and its 4,4'-dimethyl derivative by potassium peroxodisulphate in aqueous solution has been investigated by Irvine [3]. These reactions were followed under conditions where pseudo-first-order kinetics were applied and a departure from such kinetics was observed between 20 and 30% reaction. The second order rate constants were calculated from the pseudo-first-order constants. The author assumed the first order reaction with respect to both reagents, and has given an experimental equation to express the rate constant which depends upon the standard-redox-potential difference between the peroxodisulphate and complex ion couples.

Burgess and Prince [4] studied the kinetics of the oxidation of several substituted tris-1,10-phenanthroline and tris-2,2'-bipyridyl complexes of iron(II) by peroxodisulphate. They determined the activation energy and frequency factor for the particular reactions and discussed the substituent effects on these parameters. These authors obtained a linear dependence of the activation energy versus the frequency factor logarithm.

Raman and Brubaker [5] re-examined the aforesaid reaction and found the possibility of ion-pairs formation in the reaction medium. The lowering of the secondary rate constant during the reaction course was assigned to the presence of an equilibrium between the ion-pair and the $\text{Fe}(\text{II})$ and $\text{S}_2\text{O}_8^{2-}$ ions. The ion-pair then undergoes decomposition producing

the $\text{Fe}(\text{III})$ complex, the sulphate ion and the sulphate radical.

According to the Burgess and Prince [6] statement, there is little evidence for ion-pairing in aqueous solution with the large, substitution-inert cations $[\text{Fe}(\text{L}_2)_3]^{2+}$ where $\text{L}_2 = 2,2'$ -bipyridyl, 1,10-phenanthroline or their derivatives. These authors suggested that for complexes containing strongly electron-withdrawing nitro- or sulphonato-substituents, the reaction proceeds by parallel oxidation and dissociation rate-determining steps, according to the equation:

$$-\frac{d(\text{complex})}{dt} = k_1(\text{complex}) + k_2(\text{complex}) \cdot (\text{S}_2\text{O}_8^{2-})$$

The same equation was applied for the description of the reaction of iron(II) Schiff-base complexes with peroxodisulphate in acidic and basic solutions [7] and in the t-butyl alcohol-water mixtures [8].

Up to date, the ferroin oxidation reaction with peroxodisulphate has been investigated at a large peroxodisulphate excess. In the present study, the role of Ag^+ ions in the ferroin oxidation reaction with peroxodisulphate in a neutral medium has been examined and the stoichiometry of this process investigated.

Experimental

Reagents

All reagents were of analytical purity grade, and the water was triply distilled. The 0.01 M stock solution of $\text{Fe}(\text{phen})_3^{2+}$ was prepared by dissolving an appropriate amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1,10-phenanthroline in water. The ferrous sulphate was crystallized from ethyl alcohol and the presence of ferric ions was examined by the rhodanate test.

The 0.1 M solution of $\text{K}_2\text{S}_2\text{O}_8$ or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and of AgNO_3 were prepared from appropriate samples, and the required concentration was achieved by dilution. The peroxodisulphate solutions are unstable, and thus the fresh solutions were prepared for each

measuring series. Identical kinetic results were obtained when using the potassium and ammonium peroxodisulphate, respectively.

The ionic strengths were maintained with the use of sodium sulphate solution.

Analysis

The stock ferroin solution was determined by titration of 0.01 M Ce(SO₄)₂ in acid medium. Peroxodisulphate solution was standardized by reaction with excess of potassium iodide and titration of the iodine produced against a standard sodium thiosulphate solution. The peroxodisulphate concentration in the post-reaction mixture was determined as follows: the solid NaClO₄ was first added, and after a partial precipitation of the Fe(II) and Fe(III) complexes occurred the mixture was filtered off. Next, KI was added to the filtrate and this latter was then titrated with the thiosulphate solution. Such a procedure facilitates the observation of colour changes of the starch indicator.

Kinetic Measurements

Kinetic measurements were carried out at 293, 303, and 313 K, in a water thermostat equipped with a contact thermometer. The ferroin concentration was followed on a SPECOL spectrophotometer at the wavelength $\lambda = 510$ nm. In all cases the oxidized forms had a negligible absorption. Each reaction run was repeated 3 times, and the difference never exceeded 6%.

Results and Discussion

Up to now it has been assumed that the oxidation reaction of ferroin with peroxodisulphate follows the equation:



Using the redox potentials given by Irvine [3]:

$$E_{\text{O}} \text{SO}_4^{2-}/\text{S}_2\text{O}_8^{2-} = 2.01\text{V} \text{ and } E_{\text{O}} \text{Fe}(\text{phen})_3^{2+}/\text{Fe}(\text{phen})_3^{3+} = 1.14\text{V}$$

the equilibrium constant $K = 3.10^{29}$ at 298 K has been calculated by the present author. This means that the oxidation reaction of ferroin with peroxodisulphate should practically be irreversible. However, at the stoichiometric conditions and at the concentration of ferroin and peroxodisulphate equal to $5 \cdot 10^{-5}$ M and $2.5 \cdot 10^{-5}$ M, respectively, the reaction attained no more than 40% complete reaction. At the presence of $2.5 \cdot 10^{-7}$ M of Ag⁺ ions the reaction achieved 50%, and at ten times higher concentration of Ag⁺ ions the reaction still attained only 60%. At a doubled peroxodisulphate excess (i.e., at the ferroin: peroxodisulphate molar ratio of 1:1) the reaction ceased at 70%,

while at the presence of Ag⁺ in $2.5 \cdot 10^{-7}$ (or higher) concentration the reaction reached its end.

The overall reaction order for the molar concentration of reagents in the presence of Ag⁺ ions was found as 3/2, whereas its order with respect to ferroin was zero.

For the reaction carried out in stoichiometric conditions, the square root of ferroin concentration when plotted against time gives a straight line which indicates a three-halves order reaction course (Fig. 1). For the reaction carried out at peroxodisulphate excess the plot of product concentration against time is a straight line, which indicates zero order with respect to the complex concentration (Fig. 2). In the latter diagram, however, the different slopes of the three lines obtained for different initial ferroin concentrations indicate the complicated nature of the ferroin oxidation reaction with peroxodisulphate in the presence of Ag⁺ ions.

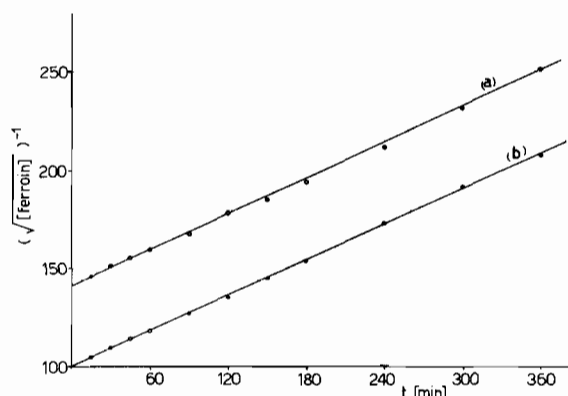


Fig. 1. Straight-linear dependence of $1/\sqrt{\text{ferroin}}$ vs. time showing the three-halves order of reaction in stoichiometric conditions.

a. $[\text{Fe}(\text{phen})_3^{2+}] = [\text{S}_2\text{O}_8^{2-}] = 5 \cdot 10^{-5}$ M; $[\text{Ag}^+] = 2.5 \cdot 10^{-7}$ M

b. $[\text{Fe}(\text{phen})_3^{2+}] = [\text{S}_2\text{O}_8^{2-}] = 1 \cdot 10^{-4}$ M; $[\text{Ag}^+] = 5 \cdot 10^{-7}$ M

The author's attempts to determine the order with respect to peroxodisulphate failed, because in the excess of ferroin it appeared impossible to determine currently the peroxodisulphate concentration.

The order with respect to Ag⁺ ions was found as 1/2. At Ag⁺ concentrations higher than 10^{-6} M the overall reaction order decreased, and at the concentration of Ag⁺ equal to $5 \cdot 10^{-6}$ M achieved the value of 1/2.

Experimental data for the Ag⁺ concentration range of ca. 10^{-7} M fulfilled the following three-halves-order equation:

$$\frac{dx}{dt} = k_{\text{obs}}(a_0 - x)^{3/2} \quad (1)$$

where: a_0 = initial ferroin concentration, x = product concentration. The rate constant values for various Ag⁺ concentrations at various temperatures are given in Table I.

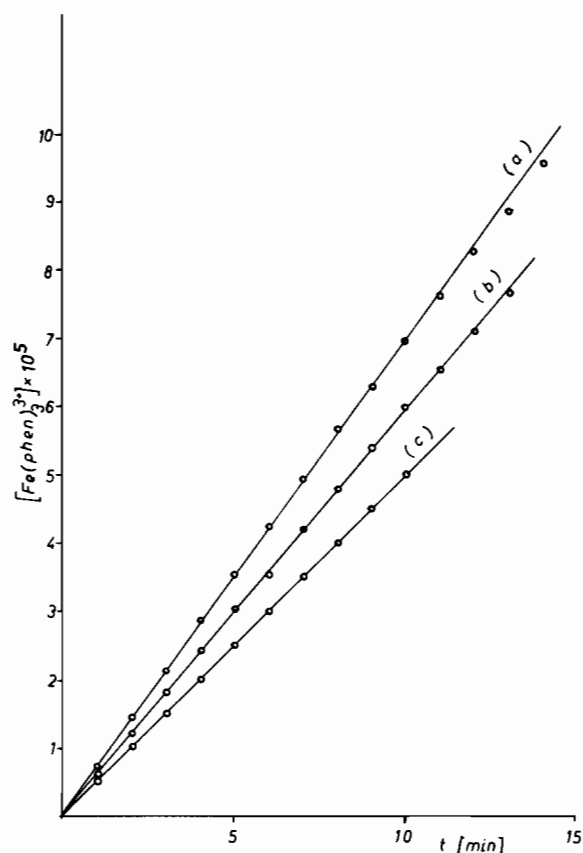


Fig. 2. Straight-linear dependence of the product concentration vs. time showing zero order of reaction at peroxodisulphate excess.

$$[\text{S}_2\text{O}_8^{2-}] = 2.425 \cdot 10^{-3} \text{ M}; [\text{Ag}^+] = 5 \cdot 10^{-7} \text{ M}$$

$$[\text{Fe}(\text{phen})_3^{2+}] = 1.5 \cdot 10^{-4} \text{ M (a)}, 1 \cdot 10^{-4} \text{ M (b)} \text{ and } 5 \cdot 10^{-5} \text{ M (c)}.$$

TABLE I. Rate Constant Values. $[\text{Fe}(\text{phen})_3^{2+}] = [\text{S}_2\text{O}_8^{2-}] = 5 \cdot 10^{-5} \text{ M}$.

Run	T	$10^7 \cdot [\text{Ag}^+]$ M	$10^3 \cdot k_{\text{obs}}$ $\text{M}^{-1/2} \cdot \text{s}^{-1}$	$\frac{k_{\text{obs}}}{\sqrt{[\text{Ag}^+]}}$
1	293 K	2.5	6.02	12.04
2		5.0	8.94	12.64
3		1.25	7.13	20.17
4	303 K	2.5	10.20	20.4
5		5.0	14.8	20.9
6		7.5	18.1	20.9
7	313 K	10.0	20.8	20.8
8		2.5	17.1	34.2
9		5.0	23.9	33.8

The k_{obs} values, when divided by the square-root of the Ag^+ concentration, give constant values for a particular temperature. This seems to confirm the half-order reaction with respect to the catalyst.

Activation energy, as determined graphically from the temperature dependence of rate constant values,

was $40 \pm 2 \text{ kJ/mol}$ and appeared lower than the respective E_A value found for the non-catalyzed process (56.5 kJ/mol [4]).

The influence of ionic strength on the rate of catalytic oxidation of ferroin was examined in the Na_2SO_4 medium. The rate constants for various Na_2SO_4 concentrations are given in Table II.

TABLE II. Influence of Na_2SO_4 Concentration on the Reaction Rate at 313 K. $[\text{Fe}(\text{phen})_3^{2+}] = [\text{S}_2\text{O}_8^{2-}] = 5 \cdot 10^{-5} \text{ M}$, $[\text{Ag}^+] = 5 \cdot 10^{-7} \text{ M}$.

Run	Na_2SO_4 M	$10^3 \cdot k_{\text{obs}}$ $\text{M}^{-1/2} \cdot \text{s}^{-1}$	μ
1		23.9	0.00035
2	0.005	14.5	0.015
3	0.01	11.2	0.03
4	0.02	7.9	0.06
5	0.03	6.21	0.09
6	0.04	5.37	0.12
7	0.05	4.64	0.15
8	0.1	3.42	0.30
9	0.15	2.88	0.45

These values obey the Brønsted-Bjerrum equation in a wide concentration range of Na_2SO_4 (Fig. 3). Extrapolation to zero ionic strength gives the value of $k_0 = 2.6 \cdot 10^{-2} \text{ M}^{-1/2} \cdot \text{s}^{-1}$, and the line slope is -2.08 ; this latter is in fair agreement with the slope of -2 theoretically expected for the reaction between oppositely charged bivalent and univalent ions ($\text{S}_2\text{O}_8^{2-}$ and Ag^+).

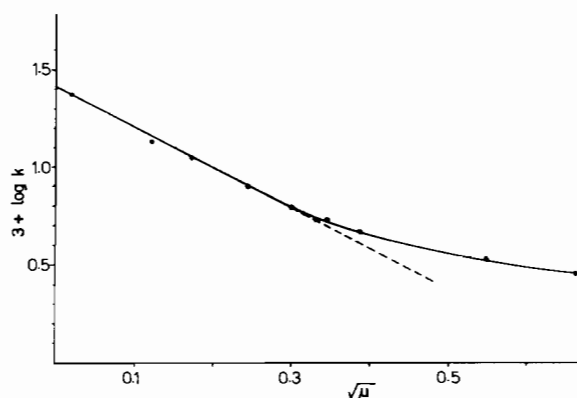


Fig. 3. Plot of $\log k_{\text{obs}}$ vs. $\sqrt{\mu}$.

The determined zero order with respect to ferroin confirms the assumption that in the catalytic process the reaction between $\text{S}_2\text{O}_8^{2-}$ and Ag^+ ions is the rate-determining step.

From the published data it is known that the peroxodisulphate oxidation at the presence of silver ions very often occurs with a zero order in reductor [9–11].

The lowering of the overall order with increasing catalyst concentration indicates that the oxidation process may have proceeded by two parallel pathways, according to the kinetic equation:

$$-\frac{d[\text{Fe(phen)}_3^{2+}]}{dt} = k_1 \cdot [\text{S}_2\text{O}_8^{2-}] + k_2 \cdot [\text{Fe(phen)}_3^{2+}] \cdot [\text{S}_2\text{O}_8^{2-}] \quad (2)$$

where $k_1 = k \cdot [\text{Ag}^+]$.

The solution of this equation would be very simple if parallel reactions could be reduced to the same order. At high excess of the ferriin, however, it is difficult to measure precisely by simple and fast means the current concentration of peroxodisulphate. On the other hand it is easy to lower the order of both reactions by studying them at a peroxodisulphate excess. The eqn. (2) would thus be:

$$-\frac{d[\text{Fe(phen)}_3^{2+}]}{dt} = k'_1 + k'_2 \cdot [\text{Fe(phen)}_3^{2+}] \quad (3)$$

and after its integration:

$$\ln \frac{k'_1 + k'_2 \cdot [\text{Fe(phen)}_3^{2+}]_0}{k'_1 + k'_2 \cdot [\text{Fe(phen)}_3^{2+}]_t} = k'_2 \cdot t \quad (4)$$

where: $[\text{Fe(phen)}_3^{2+}]_0$ and $[\text{Fe(phen)}_3^{2+}]_t$ are the initial and the current ferriin concentrations, respectively.

The reactions were carried out at a constant peroxodisulphate excess and a constant Ag^+ ions concentration, but at three different initial concentrations of the complex. From the experimental results the dependence of degree of change ($x' = x/a_0$) versus time was plotted, and then the contributions of the catalyzed and non-catalyzed reactions (as well as their respective k'_1 and k'_2 constants) were calculated. The following values have been obtained: $k'_1 = 4 \cdot 10^{-6} \text{ M} \cdot \text{min}^{-1}$, and $k'_2 = 2.2 \cdot 10^{-2} \text{ min}^{-1}$. These constants, when introduced to eqn. (4) and plotted as $\ln \{ [k'_1 + k'_2(\text{ferriin})_0] / [k'_1 + k'_2(\text{ferriin})_t] \}$ versus time, results in a straight line for different initial concentrations of the ferriin (Fig. 4).

The k'_1 and k'_2 constants divided by the peroxodisulphate concentration give the true k_1 and k_2 rate constants of eqn. (2), and these are equal to $2.75 \cdot 10^{-5} \text{ s}^{-1}$ and $0.151 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The $k_2 = 0.151$ value remains in good agreement with the $0.148 \text{ M}^{-1} \text{ s}^{-1}$ calculated by Burgess and Prince [4] for the non-catalyzed reaction.

The present results, as well as the published data cited above, suggest the following mechanism of the ferriin oxidation by peroxodisulphate at the presence of Ag^+ ions:

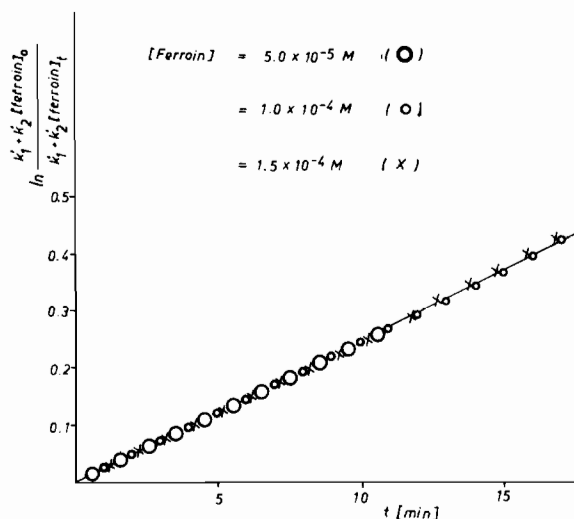
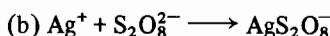
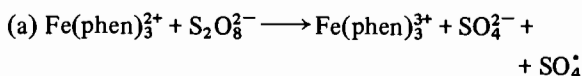
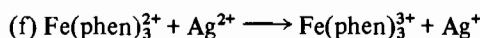
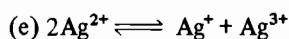
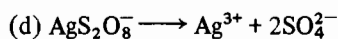
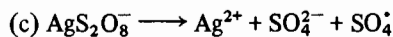


Fig. 4. Plot of $\ln \{ [k'_1 + k'_2(\text{ferriin})_0] / [k'_1 + k'_2(\text{ferriin})_t] \}$ vs. time. $[\text{S}_2\text{O}_8^{2-}] = 2.425 \cdot 10^{-3} \text{ M}$; $[\text{Ag}^+] = 5 \cdot 10^{-7} \text{ M}$



Reactions (a) and (b) are the rate-determining steps of the non-catalyzed and catalyzed reaction. Both reactions are proceeding between the oppositely charged ions: confirmed by the negative salt effect. In the non-catalyzed reaction there takes place a direct oxidation of the ferriin by peroxodisulphate via one electron transfer with the formation of Fe(phen)_3^{3+} , SO_4^{2-} , and the SO_4^{\cdot} radical. In the catalyzed reaction the one electron oxidation of Ag^+ to Ag^{2+} occurs with the formation of SO_4^{2-} and SO_4^{\cdot} . The Ag^{2+} ions may oxidize ferriin to Fe(phen)_3^{3+} or undergo disproportionation according to the reactions (f) and (e), respectively. The disproportionation ability of Ag^{2+} ion has been confirmed by the half order in Ag^+ ions. The SO_4^{\cdot} radicals may react with H_2O in further fast process, so forming OH^{\cdot} radicals. The decomposition of these latter leads to the oxygen evolution. Similar behaviour of the SO_4^{\cdot} was already postulated by Fronaeus and Ostman [12] for Ce(III) oxidation reaction with peroxodisulphate at the presence of Ag^+ ions. In the present case it is also the reaction stoichiometry which supports the aforesaid means of the SO_4^{\cdot} radical behaviour.

In the herein presented mechanism only those reactions have been taken into account, which, after a steady-state treatment, lead to the kinetic rate eqn. (2). Other possible reactions, as well as any side reactions, have not been considered.

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