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Kinetics and Mechanism of Ag (I) Catalysis in Peroxodisulphate Oxidation of Tris(2,2´-Bipyridine)Fe(II) in Aqueous Acid Media

Shazia Summer, Iftikhar Imam Naqvi* and Rasheeda Khatoon
Department of Chemistry, Jinnah University for Women, V-C, Nazimabad, Karachi-74600, Pakistan

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Abstract. The kinetics of Ag^+ catalysed oxidation of tris(2,2´-bipyridine)iron(II) complex by the peroxodisulphate ion ($S_2O_8^{2-}$) in aqueous acidic media have been investigated spectrophotometrically at λ_{max} 522 nm, the wavelength of maximum absorption of complex ion. It was determined that the rate of oxidation of $[Fe(2,2'\text{-bipyridine})_3]^{2+}$ by $S_2O_8^{2-}$ ion is independent of the concentration of $[Fe(2,2'\text{-bipyridine})_3]^{2+}$ and H^+ (within pH range of 3.8-4.8), but first order dependent with respect to the concentrations of $S_2O_8^{2-}$ and Ag^+ in the 4.16×10^{-4}–16.7×10^{-4} mol/dm^3 and 4.16×10^{-5}–16.7×10^{-5} mol/dm^3 ranges, respectively. Experimental results confirm the validity of the suggested mechanism.

Keywords: kinetics, catalysis, persulphate, tris(2,2´-bipyridine)iron(II)

Introduction

The peroxodisulphate anion ($S_2O_8^{2-}$) having standard reduction potential of +2.1 V (Latimer, 1952), pertaining to electrode reaction, $S_2O_8^{2-} + 2e^- \Rightarrow 2\,SO_4^{2-}$, is one of the strongest oxidants (Fordham and Williams, 1951). This is noteworthy that this potential is higher than that of the redox potentials for hydrogen peroxide (H_2O_2) and permanganate anion (MnO_4^-), which are 1.8 V and 1.7 V, respectively. Despite a very high reduction potential value its reaction kinetics is extremely slow. However, in presence of some catalysts, the kinetics of $S_2O_8^{2-}$ oxidation gets significantly, enhanced due to the formation of $SO_4^{\cdot-}$ radicals. Some of these catalysts include Ag (I), Mn (II), Cu (II), Cr (III) etc.

A large number of investigations regarding the kinetics of reactions involving peroxodisulphate have been reported since nineteenth century. The role of Ag (I) ion in peroxodisulphate oxidations was extensively focused by many researchers. Kinetics of decomposition of peroxodisulphate in presence of silver nitrate was investigated spectrophotometrically by Naim and Naqvi (1981). It has been found that the rate of decomposition of $S_2O_8^{2-}$ in presence of Ag (I) ion get enhanced greatly, and the reaction is first order dependent on the concentrations of $S_2O_8^{2-}$ and Ag^+. The reaction was postulated to proceed *via* $S_2O_8^{2-}$ and Ag^+ interaction, as shown below:

$$S_2O_8^{2-} + Ag^+ \longrightarrow SO_4^{2-} + SO_4^{\cdot-} + Ag^{2+}$$

Oxidation of several other reducing agents including oxalate, thiosulphate, Ce (IV), ammonia, ammonium ion, arsenious acid and hydrogen peroxide (House, 1962; Wilmarth and Haim, 1962) by peroxodisulphate in presence of Ag^+ ion have also been investigated and it was found that the kinetic order is first for both $S_2O_8^{2-}$ and Ag^+ but zero in reductant.

Ag^+ catalysed oxidation of carboxylic acids (Anderson and Kochi, 1969) and oxidations of alcohols and aromatic substrates (Walling and Camaioni, 1978) by $S_2O_8^{2-}$ have also been investigated and found to show the similar kinetic behaviour.

Kinetics of the influence of Ag^+ ions on the oxidation of $[Fe(1,10\text{-phen})_3]^{2+}$ by peroxodisulphate in neutral medium has been investigated by Cyfert (1983). Experiments on Ag^+ catalysed oxidation of [Co(II) EDTA] by $S_2O_8^{2-}$ have also been reported (Begum and Rasheed, 2001). Both of these researchers have shown that the oxidation reactions are independent of reductant concentrations.

However, Busari *et al*. (2008) discovered Ag^+ catalysed oxidation of methylene blue (MB) by peroxodisulphate ion in aqueous nitric acid medium to be substrate concentration dependent, who observed that the reaction is first order dependent each on Ag^+, $S_2O_8^{2-}$ and MB and proposed an outer-sphere mechanism. However, their data was insufficient to explain the role of the substrate (MB) in presence of Ag^+ and $S_2O_8^{2-}$.

The present investigation has been undertaken to fix the role of substrate $[Fe(2,2'\text{-bipyridine})_3]^{2+}$ in the Ag^+ catalysed oxidation by peroxodisulphate ($S_2O_8^{2-}$). The influence of various factors such as concentration of reagents, pH and ionic strength (μ) of medium, on the rate of oxidation are also being reported. This work is in continuation to our investigations pertaining to the

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*Author for correspondence; E-mail: Iftikhar.imam@yahoo.com role of Mn(II) and Co(II) as catalysts on oxidations by persulphate.

Materials and Methods

Chemicals and solutions. All chemicals including potassium peroxodisulphate ($K_2S_2O_8$), silver nitrate ($AgNO_3$), sodium acetate (CH_3COONa), acetic acid (CH_3COOH), and sodium sulphate (Na_2SO_4), were of BDH (AnalaR) grade. Double distilled and deionised water was used for preparation of the solutions. For the preparation of tris(2,2´-bipyridine)iron(II) sulphate the synthetic route (Taylor and Schilt, 1959) was adopted. Stoichiometry of complex was determined by mole ratio method and complex was characterised on the basis of uv/visible spectrum on Shimadzu-uv-visible spectrophotometer. Wavelength of maximum absorption was found to be 522 nm, which is in good agreement with the available literature (Pryzstas and Sutin, 1973) and the molar extinction coefficient was determined to be 7876.8 $dm^3/mol/cm$ (Summer *et al*., 2009).

Solution of silver nitrate was prepared by adding measured quantities of silver nitrate in acidic buffer media. Standard solutions of potassium peroxodisulphate ($K_2S_2O_8$) were prepared freshly before use to avoid any decomposition and by dissolving known quantities of reagent into deionised water. Solutions of sodium sulphate, acetic acid and sodium acetate were also prepared in deionised water.

Kinetic measurements. The kinetic study of oxidation of $[Fe(2,2'\text{-bipyridine})_3]^{2+}$ by $S_2O_8^{2-}$ catalysed by Ag^+ ion was carried out under the conditions in which concentration of oxidant $S_2O_8^{2-}$ were taken 10, 20, 30 and 40 times greater than the corresponding iron (II) complex $[Fe(2,2'\text{-bipy})]^{2+}$. Sodium acetate–acetic acid buffer was used to maintain the pH of the solution in the range of 3.8-4.8. Na_2SO_4 was used to maintain the ionic strength (μ) of the medium in the range 0.1-1.0 mol/dm^3. Various ratios of $[Fe(2,2'\text{-bipyridine})_3]^{2+}$, $S_2O_8^{2-}$ and Ag^+ were mixed in a 1 cm quartz cell to a total volume of 3 mL.

The absorbance was monitored spectrophotometrically as a function of time for each set of reaction mixture at 522 nm, the wavelength of maximum absorption of $[Fe(2,2'\text{-bipyridine})_3]^{2+}$. Kinetic data was collected by using integration method, by plotting ln (A_t-A_∞) *versus* time. All the plots were found to be straight line with intercept. The temperature of the reaction mixture was controlled to 303K, by using Techne TE-8J, thermostat bath.

Results and Discussion

In preliminary examinations it was observed that the rate of oxidation of iron (II) complex ion by $S_2O_8^{2-}$ was very slow in absence of Ag^+ ion. It was experimental that at fixed concentrations of $[Fe(2,2'\text{-bipy})_3]^{2+}$ and $S_2O_8^{2-}$ at 4.16×10^{-5} and 4.16×10^{-4} mol/dm^3, respectively, an increment in the concentration of the Ag^+ ion in the reaction mixture in the range 4.16×10^{-5}-16.7×10^{-5} mol/dm^3, significantly, increases the rate of oxidation, of $[Fe(2,2'\text{-bipy})_3]^{2+}$ by $S_2O_8^{2-}$ (Table 1).

When the values of k_{obs} for different sets of experiments were plotted as a function of concentration of Ag (I), (Fig. 1) a straight line was obtained passing through the origin. From the slope of line, the value of second order rate constant k´ was calculated to be 21.85 $dm^3/mol/s$.

Table 1. Dependence of *pseudo* first order rate constant (k_{obs}) on [Ag^+]

$[Ag^+]\times10^5$ mol/dm^3	k_{obs} $10^4/s$
4.16	9.0
8.33	18.2
12.5	28.0
16.7	36.0

$[Fe(2,2'\text{-bipy})_3]^{2+}=5.0\times10^{-5}$ mol/dm^3; $[S_2O_8^{2-}]=4.16\times10^{-4}$ mol/dm^3; pH=4.2; μ=0.5 mol/dm^3; T=303K.

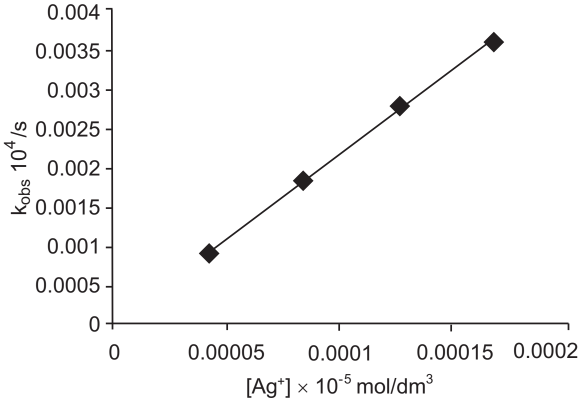

Fig. 1. Plot of *pseudo* first order rate constant (k_{obs}) *versus* [Ag^+].

To study the effect of $S_2O_8^{2-}$ concentration on the rate of reaction, kinetic runs were carried out at constant concentration of $[Fe(2,2'\text{-bipy})_3]^{2+}$ and Ag^+ at 5.0×10^{-5} and 4.16×10^{-5} mol/dm^3, while the concentration of $S_2O_8^{2-}$ was varied in the range 4.16×10^{-4}-16.7×10^{-4} mol/dm^3. It was observed that increasing concentration of peroxodisulphate ion also increases the value of k_{obs}. When these values of k_{obs} for different sets of experiments were plotted as a function of concentration of $S_2O_8^{2-}$ (Fig. 2 and Table 2), a straight line was obtained passing through the origin. From the slope of line, the value of second order rate constant k′ was calculated to be 2.363 dm^3/mol/s.

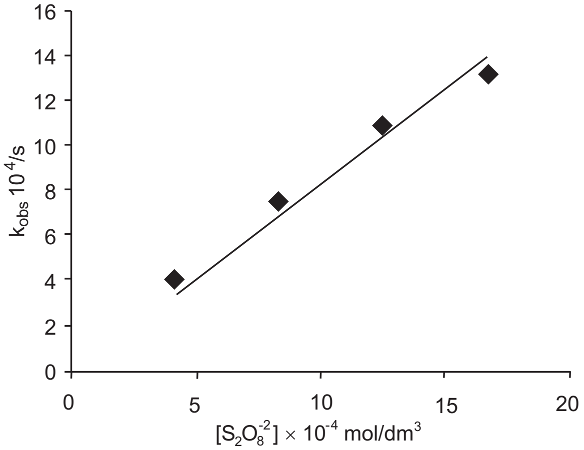

Fig. 2. Plot of *pseudo* first order rate constant (k_{obs}) *versus* $[S_2O_8^{2-}]$.

Table 2. Dependence of *pseudo* first order rate constant (k_{obs}) on $[S_2O_8^{2-}]$

$[S_2O_8^{2-}] \times 10^4$ mol/dm^3	k_{obs} 10^4/s
4.16	9.5
8.33	20.7
12.5	30.0
16.7	38.7

$[Fe(2, 2'\text{-bipy})_3]^{2+}=5.0\times10^{-5}$ mol/dm^3; $[Ag^+]=4.16\times10^{-5}$ mol/dm^3; pH=4.2; μ=0.5 mol/dm^3; T=303K.

The complex concentration was varied between (1.0×10^{-5}-5.0×10^{-5} mol/dm^3) at different pH (3.8-4.8) by keeping the concentration of $S_2O_8^{2-}$ and Ag^+ constant at 4.16×10^{-4} and 4.16×10^{-5} mol/dm^3, respectively. Graphs of ln (A_t-A_∞) *versus* time were plotted which show that there is no change in the value of rate constant. It means that change in concentration of complex does not influence the rate constant of oxidation of complex ion by peroxodisulphate (Table 3).

Table 3. Dependence of *pseudo* first order rate constant (k_{obs}) on $[Fe(2, 2'\text{-bipy})_3]^{2+}$

$[Fe(2, 2'\text{-bipy})_3]^{2+}\times10^5$ mol/dm^3	k_{obs} 10^4/s
1.0	1.9
2.0	2.0
3.0	1.9
4.0	2.0
5.0	2.0

$[S_2O_8^{2-}]=4.16\times10^{-4}$ mol/dm^3; $[Ag^+]=4.16\times10^{-5}$ mol/dm^3; pH=4.2; μ=0.5 mol/dm^3; T=303K.

It has been observed that the rate is also independent of the hydrogen ion concentration in the pH range of 3.8 to 4.8 (Table 4).

Table 4. Dependence of *pseudo* first order rate constant (k_{obs}) on $[H^+]$

pH	k_{obs} 10^4/s
3.8	2.0
4.2	2.0
4.4	1.5
4.6	2.0
4.8	2.0

$[Fe(2, 2'\text{-bipy})_3]^{2+}=5.0\times10^{-5}$ mol/dm^3; $[S_2O_8^{2-}]=4.16\times10^{-4}$ mol/dm^3; $[Ag^+]=4.16\times10^{-5}$ mol/dm^3; μ=0.5 mol/dm^3; T=303K.

The dependence of the rate constant on the ionic strength (μ) of the medium was also studied by changing the ionic strength (0.1-1.0 mol/dm^3) using Na_2SO_4, while the remaining parameters were kept constant.

The plot of log k *versus* $(\mu)^{1/2}$ (Fig. 3 and Table 5) was linear with a negative slope of -1.85. Negative slope shows that the reactants bear opposite charges. As the reaction depends on $S_2O_8^{2-}$ and Ag^+, which carry -2 and +1 charges, respectively. Therefore, the resulting product of charges is suggested to be -2. The results obtained by using Debye Huckel limiting law, $\log k = \log k_o + 1.02\, z_A z_B (\mu)^{1/2}$ are consistent with this value.

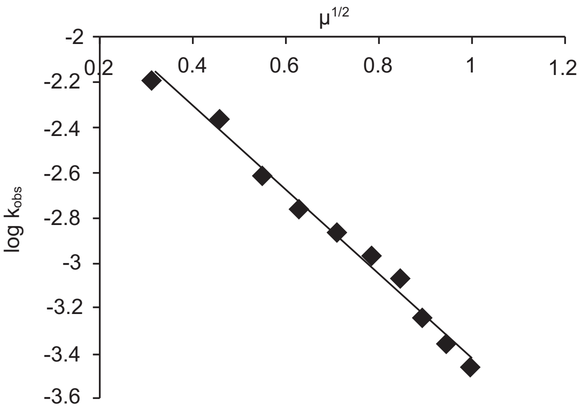

Fig. 3. Plot of log k *versus* $(\mu)^{1/2}$.

Proposed mechanism for the Ag^+ catalysed oxidation of $[Fe(2,2'\text{-Bipy})_3]^{2+}$ by $S_2O_8^{2-}$. On the basis of present investigations and the cited literature mentioned earlier, the mechanism is suggested to incorporate the following steps:

Table 5. Variation of log k *versus* (μ)½

μ(Na_2SO_4) mol/dm³	k×10³ mol/dm³/s	μ½	log k
0.1	6.61	0.316	-2.18
0.2	4.17	0.447	-2.38
0.3	2.51	0.548	-2.60
0.4	1.78	0.632	-2.75
0.6	1.05	0.774	-2.98
0.7	0.83	0.837	-3.08
0.8	0.58	0.894	-3.24
0.9	0.46	0.949	-3.34
1.0	0.36	1.00	-3.45

$[Fe(2,2'\text{-bipy})_3]^{2+}=5.0\times10^{-5}$ mol/dm³; $[S_2O_8^{2-}]=4.16\times10^{-4}$ mol/dm³; $[Ag^+]=4.16\times10^{-5}$ mol/dm³; μ=0.5 mol/dm³; T=303K.

$$Ag^+ + S_2O_8^{2-} \xrightarrow{\text{slow}} [Ag_2S_2O_8]^{-1} \ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

$$[Ag_2S_2O_8]^{-1} \xrightarrow{\text{fast}} Ag^{2+} + SO_4^{2-} + SO_4^{1-} \ldots\ldots\ldots\ldots\text{(ii)}$$

$$SO_4^{1-} + Ag^+ \xrightarrow{\text{very fast}} Ag^{2+} + SO_4^{2-} \ldots\ldots\ldots\ldots\ldots\ldots\text{(iii)}$$

$$[Fe(2,2'\text{-bipy})_3]^{2+} + Ag^{2+} \xrightarrow{\text{fast}}$$
$$[Fe(2,2'\text{-bipy})_3]^{3+} + Ag^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(iv)}$$

Equation (i) represents the slow association of $S_2O_8^{2-}$ and Ag^+ ions, which results in formation of an ion pair $[Ag_2S_2O_8]^{-1}$. The next equation (ii) involves the decomposition of this ion pair into Ag^{2+}, SO_4^{2-} and SO_4^- is likely to be a faster one. The transient species SO_4^- generated in equation (ii), oxidises Ag^+ ion as shown in equation (iii), this step as involving the transient species, is also fast. Equation (iv) shows the regeneration of Ag^+ by the fast reduction of Ag^{2+} by the $[Fe(2,2'\text{-bipy})_3]^{2+}$ ion.

In the above suggested mechanism, equation (i) represents the rate determining step since the oxidation rate is first order with respect to the concentrations of both Ag^+ and $S_2O_8^{2-}$ ions and hence the rate of formation of product would depend on the concentration of these ions.

The rate equation according to equation (i) will be,

$$\text{Rate} = k'[Ag^+][S_2O_8^{2-}] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(v)}$$

where:

k´ = the second order rate constant, having the value 56810 dm³/mol/s.

The above proposed mechanism is also supported by the plots of k_{obs} against Ag^+ ion concentration and that of k_{obs} against $S_2O_8^{-2}$ concentration (Begum and Rasheed, 2001). These are straight line plots. In the first case the slope divided by $S_2O_8^{-2}$ concentration gives k´=52526 dm³/mol/s, whereas, in second case slope divided by Ag^+ ion concentration gives k´=56810 dm³/mol/s. The values of these second order rate constants are in good agreement with each other and strongly support first order dependence of reaction rate individually on Ag^+ and $S_2O_8^{2-}$ ion concentrations.

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