

The effect of light on the Mn(II) or Fe(III)-catalyzed oxidation of aqueous S(IV)

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Abstract— In absence of light, the reaction kinetics of Mn(II) and Fe(III)-catalyzed oxidation of S(IV) in unbuffered and buffered solutions were studied. An activation energy of $77.4 \text{ kJ} \cdot \text{mol}^{-1}$ for the Mn(II)-catalyzed oxidation of S(IV) is obtained. On the basis of the investigation of the catalytic effects of Mn(II) and Fe(III) on the oxidation of S(IV), it has been elucidated that the catalytic activity of Mn(II) is greater than that of Fe(III), and that Mn(II) and Fe(III) do not have a significant synergic effect on the catalytic oxidation of S(IV). The catalytic oxidation and autooxidation of S(IV) in unbuffered solution was also explored in the presence of light. The results show that the reaction is first order with respect to S(IV) concentrations, the reaction rate increases with increasing light intensity and the concentrations of Fe(III) and Mn(II), and that the photoassisted catalytic activity of Fe(III) is greater than that of Mn(II).

Keywords: photoassisted catalytic activity; aqueous S(IV); reaction kinetics.

1 Introduction

The autooxidation of S(IV) by dissolved oxygen in pure water is very slow. However, the trace quantities of catalytic metal ions Mn(II), Fe(III) and so on existing in the liquid phase of the atmosphere can speed up the oxidation process. The effect of metal ions on the transformation of S(IV) into S(VI) is dependent on their activity and concentration in the liquid phase. Because Mn(II) and Fe(III) exist in the atmosphere with higher concentrations, the reaction kinetics of the Mn(II) and Fe(III)-catalyzed oxidation of S(IV) have widely been studied but there is still a considerable amount of disagreement. Cohn *et al.* (Cohn, 1980) considered that the catalytic activity of Fe(III) is greater than that of Mn(II), while Penkett *et al.* (Penkett, 1979) suggested that there is an effect of Mn(II) on the oxidation of S(IV) but Fe(III) does not significantly reveal catalytic property. A very interesting problem is whether

a synergic catalytic effect of Fe(III) + Mn(II) on the oxidation of S(IV) exists, which has not been solved thus far.

The influence of ultraviolet light from solar radiation on the oxidation of S(IV) in liquid phase has been noted. Dogliotii and Hayon (Dogliotii, 1967; Hayon, 1972) have investigated the photolysis reaction of S(IV). Lunak and Veprek-Siska (Lunak, 1976) have studied the Fe(III)-catalyzed photooxidation of SO_3^{2-} , determined the quantum yields of light for several wavelengths, and pointed out that the quantum yields are dependent on the wavelengths of irradiation and the concentrations of Fe(III) in the system. They have also proposed that a quantum of light is absorbed by a Fe(III)- SO_3 complex. However, the reaction system studied and the wavelengths of light used by these researches are distinctly different from the conditions of the real atmosphere.

The work presented here studied the reaction kinetics of Mn(II) and Fe(III)-catalyzed oxidation of S(IV) in both the absence and the presence of light.

2 Experimental

The water used in the experiment was tridistilled. The S(IV) was prepared with analytical reagent sodium sulfite, and the metal ions Mn(II) and Fe(III) as catalysts were prepared with manganous sulfate and ferric sulfate, respectively. The light source was GGZ-typical straight tube High Pressure Mercury Lamp of 120 W. The schematic diagram of the apparatus used in the experiment is shown in Fig. 1 (Xu, 1987).

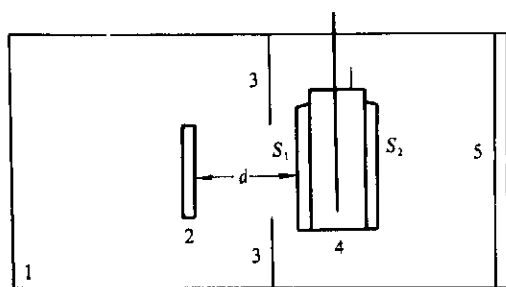


Fig. 1 Schematic diagram of the reaction equipment
 1— wooden box; 2— high pressure mercury lamp; 3— plate; 4— reactor; 5— black paper; S_1 , S_2 — reactor surfaces; d — distance between lamp and S_1

The purified air was bubbled into the water used in the experiment about one hour before the reaction occurred. If the photoassisted experiments were done, the light intensity would be kept constant for 15 minutes before reaction. During the reaction, the samples were taken by pipette over a predetermined time, and the S(IV) concentrations were then analyzed by hydrochloride acid paraffine spectrophotometry (72-typical spectrophotometer). The light intensity was determined by J-221 typical long wavelength ultraviolet light meter (UVP Cop. America).

3 Results and discussion

3.1 Catalytic oxidation of S(IV) by Mn(II) in absence of light

The Mn(II)-catalyzed oxidation of S(IV) was carried out in two different systems; unbuffered solution and potassium phosphate buffered solution. The typical reaction curves are shown in Fig. 2.

Ibusuki *et al.* (Ibusuki, 1984) have pointed out that the reaction of the Mn(II) catalyzed oxidation of S(IV) is zero order with respect to dissolved oxygen concentrations but there are still some controversies about the orders of Mn(II) and S(IV) concentrations. We assumed a kinetic equation of reaction as follows:

$$-\frac{d[S(IV)]}{dt} = k[Mn(II)]^m[S(IV)]^n. \quad (1)$$

Because the Mn(II) concentrations, bubbling rate, agitating rate and temperature were controlled all the same in each experiment, Equation(1) can be written as

$$-\frac{d[S(IV)]}{dt} = k_r[S(IV)]^n. \quad (2)$$

Determining the value of n , we used the graphic method of the initial concentrations in buffered solution of pH=5.89. The initial reaction rate was replaced by the mean rate in the initial reaction time interval of 0–0.5 min. Taking the natural logarithm to both sides of Equation (2), it can be rewritten as follows:

$$\ln \left\{ -\frac{[S(IV)]_{0.5} - [S(IV)]_0}{0.5} \right\} = \ln k_r + n \ln [S(IV)]_0. \quad (3)$$

Fig. 3 is obtained by graphing $\ln \left\{ -\frac{[S(IV)]_{0.5} - [S(IV)]_0}{0.5} \right\}$ vis $\ln [S(IV)]_0$.

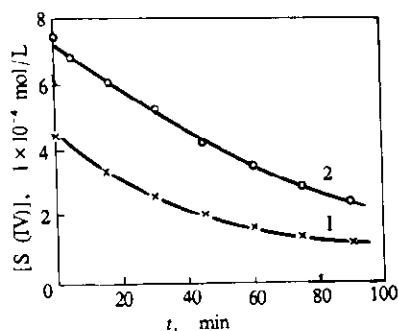


Fig. 2 Decay of [S(IV)] with time due to the Mn(II)-catalyzed oxidation of S(IV) ($T=298$ K, $[Mn(II)]=2.50 \times 10^{-6}$ mol/L 1— unbuffered solution; 2— buffered solution of pH=5.89)

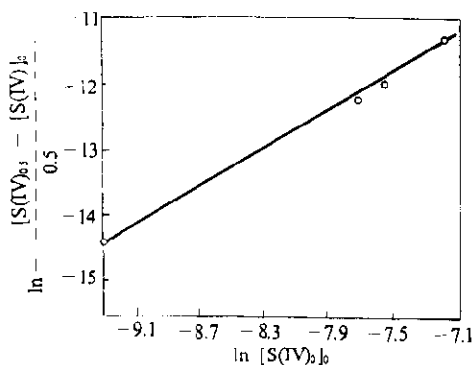


Fig. 3 Plot of $\ln \left\{ \frac{[S(IV)]_{0.5} - [S(IV)]_0}{0.5} \right\}$ vis $\ln[S(IV)]_0$
($T = 298\text{K}$, $\text{pH} = 5.89$, $[Mn(II)] = 2.50 \times 10^{-6}$ mol/L)

$$k_r = 1.47 \times 10^{-3} + 3.20 \times 10^3 [Mn(II)], \quad (\text{pH} = 5.89) \quad (5)$$

$$k_r = 5.12 \times 10^{-3} + 3.24 \times 10^3 [Mn(II)], \quad (\text{unbuffered solution}) \quad (6)$$

As known from Equation(5), if $[Mn(II)] > 10^{-6}$ mol/L, it can be considered as $k_r = k[Mn(II)]$. This is consistent with the results obtained by Ibusuki and Barnes in $[Mn(II)]$ of $1 \times 10^{-6} - 5 \times 10^{-6}$ mol/L.

The effect of temperature on the reaction rate of the catalytic oxidation of S(IV) by Mn(II) has been studied. A linear plot is obtained when the log of the 3/2th order rate constant is plotted against the inverse absolute temperature (Fig. 4). The slope of this line gives an activation energy (E_a) of $77.7 \text{ kJ} \cdot \text{mol}^{-1}$ for the oxidation ($\text{pH} = 5.89$). A result given by Ibusuki and Barnes is $E_a = 74.3 \text{ kJ} \cdot \text{mol}^{-1}$ in the solution of $\text{pH} = 5.04$, $[Mn(II)] = 2.0 \times 10^{-6}$ mol/L.

3.2 Catalytic oxidation of S(IV) by Fe(III) in the absence of light

The catalytic oxidation of S(IV) in the solution containing Fe(III) has been studied in order to clarify whether the synergic

An m of $3/2$ is obtained from the slope of the straight in Fig. 3, therefore, an equation can be derived as

$$-\frac{d[S(IV)]}{dt} = k_r [S(IV)]^{3/2}. \quad (4)$$

It was previously recognized that the rate constant k_r was probably a function of Mn(II) concentrations. However, the results which a number of researchers obtained were in conflict with each other. We linearly fitted k_r to $[Mn(II)]$ and obtained the following equations in two different systems, respectively:

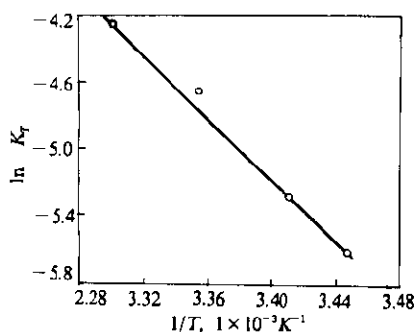


Fig. 4 Arrhenius plot for the Mn(II) catalyzed oxidation of S(IV)
($\text{pH} = 5.89$, $[Mn(II)] = 2.50 \times 10^{-6}$ mol/L)

effect of Mn(II)+Fe(III) on the catalytic oxidation of S(IV) exists. The reaction rate of the Fe(III)-catalyzed oxidation of S(IV) has been expressed as (Fuzzi, 1978)

$$\text{pH} < 4 \quad - \frac{d[\text{S(IV)}]}{dt} = k_f [\text{S(IV)}][\text{Fe(III)}], \quad (7)$$

$$\text{pH} > 5 \quad - \frac{d[\text{S(IV)}]}{dt} = k_f [\text{S(IV)}]^2 [\text{Fe(III)}], \quad (8)$$

The values of pH in our two systems were more than 5, therefore, the rate constants k_f could be obtained from Equation (8). The results show that k_f are equal to 7.64×10^{-2} and $1.15 \times 10^{-1} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ in unbuffered solution and pH=5.89 buffered solution, respectively.

3.3 Catalytic effect of Mn(II)+Fe(III) on the oxidation of S(IV) in absence of light

Based on the above experiments, the effect of Mn(II)+Fe(III) on the catalytic oxidation S(IV) has been studied. The rate constant k_m was fitted by using the 3/2th order reaction with respect to S(IV) concentrations. The results are shown in Table 1.

Table 1 The 3/2th order rate constants k_m of Mn(II)+Fe(III) catalyzed oxidation of S(IV) $\text{L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{s}^{-1}$ ($2.50 \times 10^{-6} \text{ mol/L} [\text{Mn(II)}] + 2.50 \times 10^{-6} \text{ mol/L} [\text{Fe(III)}]$, T=298 K)

Reaction systems	pH=5.89 buffered solution	Unbuffered solution
k_m	6.62×10^{-3}	6.40×10^{-3}

From the comparison of Table 1 with Equations (5) and (6), it is known that there is no synergic effect of Fe(III)+Mn(II) on the catalytic oxidation of S(IV). The rate of the Mn(II)+Fe(III) reaction is smaller than that produced using only Mn(II). It is elucidated that the catalytic activity of Mn(II) is greater than that of Fe(III). The complex effect of Mn(II) with S(IV) is weakened because of the existence of Fe(III). The synergic effect of Mn(II)+Fe(III) which was previously found is most likely due to the reagents used. For example, Barrie and Geogrii (Barrie, 1976) used MnCl_2 and FeCl_3 as catalysts. However, the effect of Cl^- on the oxidation of S(IV) had been noted (Clark, 1983).

3.4 Photoassisted autooxidation of S(IV)

Under the constant temperature, the photoassisted autooxidation of S(IV) has been studied in the absence of added metal ions. A linear plot is obtained by fitting

the first order reaction with respect to S(IV) concentrations (Fig. 5). Changing the initial S(IV) concentrations, the similar results are obtained. It follows that the reaction rate of the photoassisted autooxidation of S(IV) can be written as

$$-\frac{d[S(IV)]}{dt} = k_o[S(IV)], \quad (9)$$

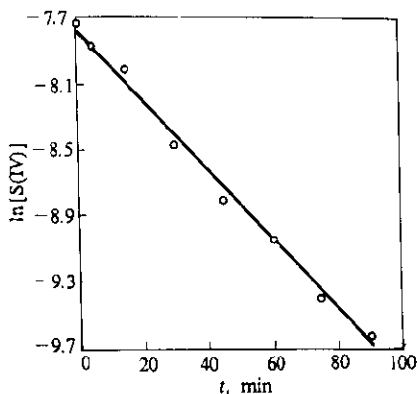


Fig. 5 Plot of $\ln[S(IV)]$ vis time
($T=298$ K, $d=15$ cm)

An average value of k_o for four replications of the experiment is $(3.52 \pm 0.196) \times 10^{-4} \text{ s}^{-1}$, which is an order of magnitude greater than that of the absence of light ($k_o = 1.0 \times 10^{-5} \text{ s}^{-1}$; Xu, 1987).

When the light intensity irradiating on the reactor surface is changed by changing the distance between light source and reactor, the light intensity absorbed by the reaction system also changes. The influence of light intensity on the rate is shown in Table 2.

3.5 Photoassisted catalytic oxidation of S(IV) by Fe(III) and Mn(II)

In the presence of added Fe(III), the obvious

Table 2 Values of $k_o (\text{s}^{-1})$ of the first order reaction for different light intensity ($T=298$ K)

Light distance, cm	Light intensity, mW cm^{-2}		k_o $10^{-4} \cdot \text{s}^{-1}$
	S ₁ surface	S ₂ surface	
27	0.96	0.48	2.58 (n=2)
21	1.50	0.60	2.80 (n=2)
15	2.70	1.00	3.52 (n=4)

effect of light on the oxidation of S(IV) was found. A linear plot is obtained when $\ln[S(IV)]$ is plotted against the reaction time. Therefore, the rate of the photoassisted catalytic oxidation of S(IV) by Fe(III) can also be written as:

$$-\frac{d[S(IV)]}{dt} = k_f'[S(IV)], \quad (10)$$

where k_f' includes not only the influence of light intensity but also Fe(III) concentra-

tions. Under the condition of constant Fe(III) concentrations, the increases of k_f' with increasing light intensity are also obtained. If the light intensity is kept constant, a linear plot is obtained when k_f' is plotted against Fe (III) concentrations (Fig. 6). The linear relationship between k_f' and Fe(III) concentrations can be expressed as:

$$k_f' = 4.12 \times 10^{-4} + 3.0 \times 10^2 [\text{Fe(III)}], \quad (11)$$

If Fe(III) was replaced by Mn(II) under constant light intensity, we obtain a first order reaction with respect to S(IV) concentrations but there is not an obvious linear relationship between k_m' and Mn(II) concentrations under constant light intensity. The values of k_m' for different Mn(II) concentrations are shown in Table 3.

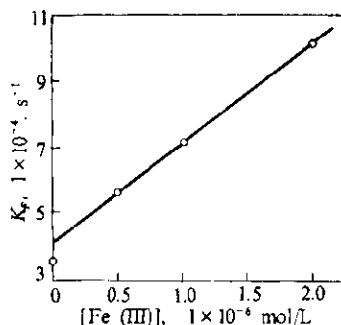


Fig 6 Dependence of k_f on [Fe(III)]
(T = 298K, d = 15 cm)

Table 3 Values of k_m' (s^{-1}) for different Mn(II) concentrations
(T = 298 K, d = 15 cm)

Mn (II) concentrations, mol/L	5.00×10^{-7}	1.00×10^{-6}	2.00×10^{-6}
$k_m', \text{ s}^{-1}$	5.24×10^{-4}	6.28×10^{-4}	6.54×10^{-4}

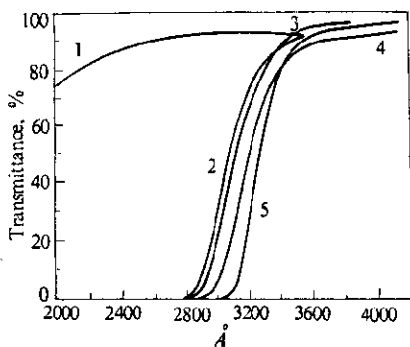


Fig. 7 Absorption curves of several kinds of glass for ultraviolet light

1— Quartz; 2— Pyrex; 3— Shanghai No.95
(Thickness of 1.45 mm); 4— Shanghai No. 95
(1.45 × 2 mm); 5— Shanghai No. 17 (2.20 mm)

Because the reactor material is the glass of Shanghai No. 95, the wavelength of light penetrated into reaction solution is above 2800 Å (Fig. 7). Fig. 8 shows the absorption spectrum of several solutions containing S(IV), Fe(III) and /or Mn(II). When S(IV) concentration reaches the value used in a reaction solution in the absence of added metal ions, it does not absorb the light of wavelength above 2800 Å. As S(IV) concentrations increase from 5.32×10^{-4} to 1.32×10^{-2} mol/L, the solution absorbs a small amount of light at wavelength above 2800 Å. The absorption spectrum is not greatly changed

although Fe(III) or Mn(II) concentrations added into the S(IV) solution of 5.32×10^{-4} mol/L have been increased to 1×10^{-6} mol/L. However, when Fe(III) concentrations increase to 5.0×10^{-5} mol/L in S(IV) solution, it can clearly be seen that

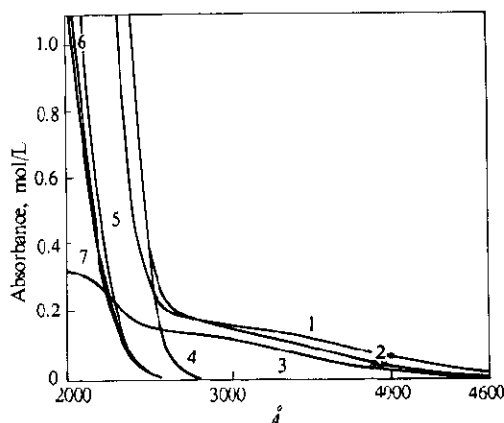


Fig. 8 Absorption curves of several reaction systems

for ultraviolet light (cell of 1 cm)

1. 9.63×10^{-3} mol/L [S(IV)] + 1.00×10^{-4} mol/L [Fe(III)];
2. 3.76×10^{-3} mol/L [S(IV)] + 5.00×10^{-5} mol/L [Fe(III)];
3. 5.00×10^{-5} mol/L [Fe(III)];
4. 1.32×10^{-2} mol/L [S(IV)];
5. 5.32×10^{-4} mol/L [S(IV)];
6. 5.32×10^{-4} mol/L [S(IV)] + 1.00×10^{-6} mol/L [Fe(III)];
7. 5.32×10^{-4} mol/L [S(IV)] + 1.00×10^{-6} mol/L [Mn(II)]

the solution absorbs much light of wavelength above 2800 \AA . According to that the solution of 3.76×10^{-3} mol/L S(IV) + 5.0×10^{-5} mol/L Fe(III) absorbs a larger amount of light at wavelength above 2800 \AA than the solution of 5.0×10^{-5} mol/L Fe(III), it can be deduced that a complex compound of S(IV) with Fe(III) may be formed. It is also asserted that the catalytic role of Fe(III) or Mn(II) in the transformation of S(IV) to S(VI) is through the complex combination of them with S(IV) (HSO_3^- or SO_3^{2-}) in thermal reaction. In thermal reaction, Barrie and Georgii (Barrie, 1978) proposed that Mn(II) complexes with SO_3^{2-} to form $[\text{Mn}(\text{SO}_3^{2-})_3]^{4-}$, while Ibusuki and Barnes (Ibusuki, 1984) considered that Mn(II) reacts with HSO_3^- to produce $[\text{Mn}(\text{II})(\text{HSO}_3^-)_2]^{2-x}$. Similarly the reaction mechanism of Fe(III)-catalyzed oxidation of S(IV) may be explained by the complex formation of Fe(III) with HSO_3^- or SO_3^{2-} .

Hayon *et al.* (Hayon, 1972) proposed that the photochemical autooxidation of SO_3^{2-} is due to the initiation of SO_3^{2-} absorbing photon. However, the wavelength of light which was used in their experiments is less than 2800 \AA , which is far away from the situation in the atmosphere. Lúnak and Veprek-Siska experiments showed that in the photoassisted catalytic oxidation of S(IV) by Fe(III) or Mn(II) the initial step of reaction is the interaction of a photon with the complex formed by the reaction of S(IV) with Fe(III) or Mn(II). This is confirmed by our experiments. As for our results about the photoassisted autooxidation of S(IV), it is considered that although Fe(III) or Mn(II) was not added into the reaction solution, some trace quantities of metal ions Mn(II), Fe(III) and so on must exist in the reaction solution. For example, the Mn(II) concentrations of 3.0×10^{-8} mol/L in pure water have been determined by Inductive Couple Plasma Emission Spectrometry.

Perhaps most interesting, however, is about the catalytic activity of Fe(III) and Mn(II). In thermal reaction, the catalytic activity of Mn(II) is greater than that of Fe(III); while in photoassisted reaction, the catalytic activity of Fe(III) is greater than that of Mn(II). This illustrates that light changes the reaction mechanism of metal ion-catalyzed oxidation of S(IV).

The reaction of the photoassisted catalyzed oxidation of S(IV) is a very complicated process. In particular, the reaction mechanism for this process needs to be studied further. Our results show that the photoassisted catalytic oxidation of S(IV) by metal ions is a pathway not to be ignored in the transformation of sulfur dioxide into sulfate in the atmosphere.

4 Conclusions

In thermal reaction, there are catalytic effects of Fe(III) or Mn(II) on the oxidation of S(IV) but Fe(III) and Mn(II) do not reveal a synergic catalytic effect on the oxidation of S(IV). The catalytic activity of Mn(II) is greater than that of Fe(III).

The reaction of Fe(III) or Mn(II)-catalyzed oxidation of S(IV) is initiated by the light wavelength above 2800Å in photoassisted reaction. The catalytic activity of Fe(III) is greater than that of Mn(II) in photoassisted reaction.

The Fe(III) or Mn(II)-catalyzed oxidation of S(IV) is an important pathway in the transformation of SO₂ into SO₄²⁻ in the atmosphere.

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