

### **C-1. 3. 2 Physico-chemical Formation Processes of Acidic and Acidifying Substances in the Atmosphere**

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**Abstract:** Photochemical oxidation of sulfite to sulfate in cloud droplets were experimentally investigated in order to assess their atmospheric significance. Photoirradiation to sulfite in Fe(III) solution of several micro molar concentration evidently accelerated the oxidation to a great extent. The photocatalytic oxidation in iron(III) solution obeyed a rate law of  $[S(IV)]^{0.5} [Fe(III)]^{0.7} [H^+]^{0.2}$ . The photocatalytic oxidation were also investigated in the suspensions of eight soil samples including Kosa and Kanto loam to find that the oxidation took place significantly in some suspensions including Kanto loam. Photocatalytic oxidation of atmospheric sulfur dioxide in the Fe(III) solutions was evaluated on the basis of rate constant obtained with solar radiation to conclude that the photocatalysis would be considerably significant in atmospheric formation of sulfuric acid in the East Asia.

**Key Words:** Sulfuric Acid, Hydrogen Peroxide, Soil Particle, Iron(III) Ion, Photochemistry

#### **1. Introduction**

Iron containing aerosol and soil particle including Kosa in the atmosphere will be significant in the atmospheric formation of acidic substances in East Asia. These particles will be associated with atmospheric droplets and photocatalytic oxidation of dissolved sulfur dioxide or sulfate could be photochemically converted to sulfuric acid in these droplets. However, no research was reported on this photooxidation so far.

In this study, photocatalytic oxidation of sulfite in these model solution and suspension were experimentally studied from the view point of reaction kinetics.

#### **2. Experimental**

Iron (III)perchlorate aqueous solution and suspension of eight soil samples including

Kosa, Kanto loam, and Aso volcanic ash were employed as reaction media. Xenon and mercury arcs and solar radiation were irradiated to these reaction systems.

### 3. Results and Discussion

#### 3.1 Photooxidation in Fe(III) solution

##### 3.1.1 Reaction Kinetics

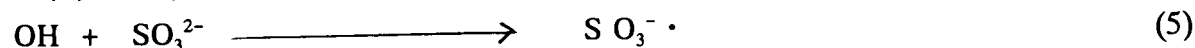
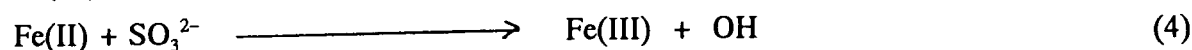
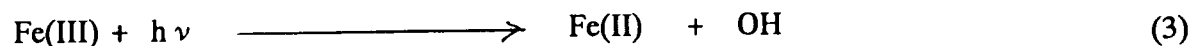
Photocatalytic oxidation of sulfite was successfully found in iron(III) aqueous solution. On the basis of determinations of reaction rates in solutions with different concentrations of sulfite, iron(III), and hydrogen ion, the rate law was found to be as follows:  $\text{rate} = k [\text{S(IV)}]^{0.5} [\text{Fe(III)}]^{0.7} [\text{H}^+]^{0.2}$ . In some runs, the reaction was likely to proceed with non-0.5th order of kinetics. The order was investigated with a large range of initial S(IV) concentrations. The 0.5th order rate constant did not vary with the initial S(IV) concentrations (Fig. 1) whereas 0.4th and 0.6th order rate constants were dependent upon the initial concentration.

##### 3.1.2 Reaction Mechanism

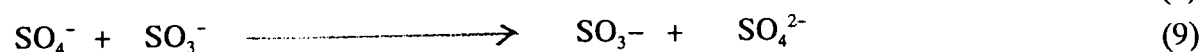
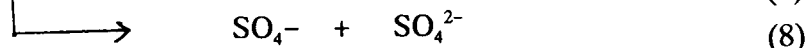
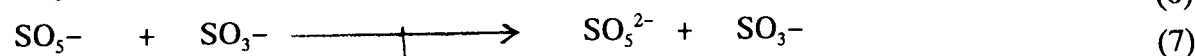
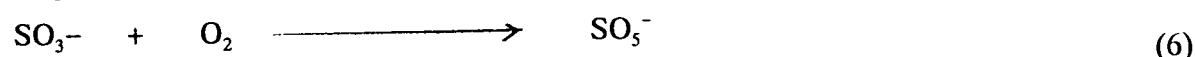
The photooxidation seemed to involve radical processes with OH radical as suggested by Graedel et al. (1985). The reaction mechanism was investigated with addition of t-butanol and benzene as free radical scavengers (Deister and Warneck; 1990, Deister et al.; 1990) to propose a free radical mechanism accounting for the 0.5th order dependence on sulfite concentration. After addition of these free-radical scavengers, the 0.5th order kinetics changed to 0.7th order. This rate constant decreased with increasing amount of added scavengers. However, the constant did not converge to zero with a large excess amount of added scavengers (Fig., 2). These behaviors were explained if one would assume the reaction proceeded via simultaneous radical and non-radical mechanism, where some complexes of S(IV) and Fe(III) species might be directly photolyzed.

The following sequence of free radical reactions would explain radical mechanisms of 0.5th order kinetics.

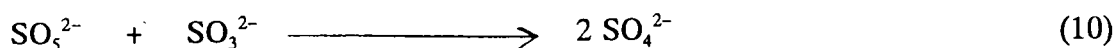
##### *Initiation:*



##### *Propagation*



### *Oxidation*



### *Termination*



#### 3.1.3 Formation and Decomposition of Hydrogen Peroxide

Photoirradiation of iron(III) solution caused hydrogen peroxide formation, and hydrogen peroxide was also photochemically decomposed if the compound is initially present. In the absence and presence of initial hydrogen peroxide, the concentration converged to a common concentration level with the photoirradiation (Fig.3).

#### 3.2 Photooxidation in soil particle suspension

Oxidation of sulfite took place in the suspensions of all the soil samples without photoirradiation. As for photocatalytic oxidation in the suspensions, some soil showed photoactivity and others not. Arizona dust did not affect the photooxidation.

Kosa and Kanto loam lowered the reaction rate. slowed the reaction. Aso volcanic dust increased the reaction rate by a factor of more than two when photoirradiated. No distinct relationships were recognized between the reaction rate and elemental composition of soil samples, which strongly suggested the thermal oxidation would be affected by factors including dissolved components and surface composition. In the case of photocatalysis, crystal structures of major components of each soil samples would also affect the oxidation rate. In the photocatalytic oxidation in suspensions, the following three factors at least would affect the reaction rate: (1)photoexcitation of catalyst species on the soil surface, (2) physical chemistry processes associated with photodissolution of iron species, and (3) homogeneous photocatalytic processes of iron species dissolved into the suspension. These factors contribute to the reaction processes to the following extension: (1): 32%, (2): 64%, and (3) 4%.

#### 3.3 Atmospheric significance of the photocatalysis

The conversion rate of  $\text{SO}_2$  in atmospheric droplet is expressed by eq. (15) where  $P_{\text{total}}(\text{SO}_2)$  and  $P_{\text{aq}}(\text{SO}_2)$  are air concentration of  $\text{SO}_2$  before the formation of atmospheric droplets and aqueous-phase concentration expressed as corresponding air concentration.

$$dP_{\text{aq}}(\text{SO}_2)/dt = -WRT k_p \{H^*/(1 + H^*WRT)\}^{0.5} P_{\text{total}}(\text{SO}_2)^{-0.5} \quad (15)$$

(W: liquid water content, R: gas constant,  $H^*$ : effective Henry's law constant, T: temperature,  $k_p$ : rate constant in the equation,  $d[S(\text{IV})]/dt = -k_p[S(\text{IV})]^{0.5}$ ).

The rate constant,  $k_p$ , was experimentally determined with irradiation of actual solar radiation (Fig. 4).

The atmospheric conversion rate was assessed by eq. (15) to be 24~27 % h<sup>-1</sup> with 1 ppb of SO<sub>2</sub>. The conversion rate in cloud droplets containing soil particles was assessed on the basis of corresponding concentrations in fog droplets to be 0.66 % h<sup>-1</sup> because measurements of soil particle concentrations in cloud droplets are not available. These quantitative evaluation strongly suggested experiment cloud droplets containing iron species will play an significant part in the atmospheric formation of sulfuric acid in East Asia.

## References

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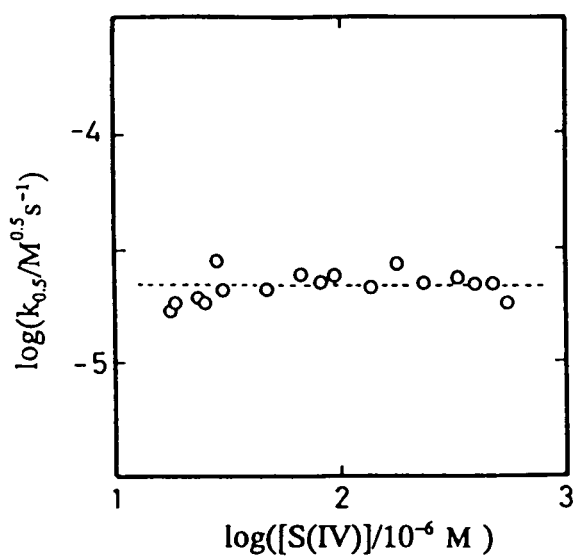


Fig. 1 0.5th order rate constant,  $k_{0.5}$  for various initial concentrations of S(IV).

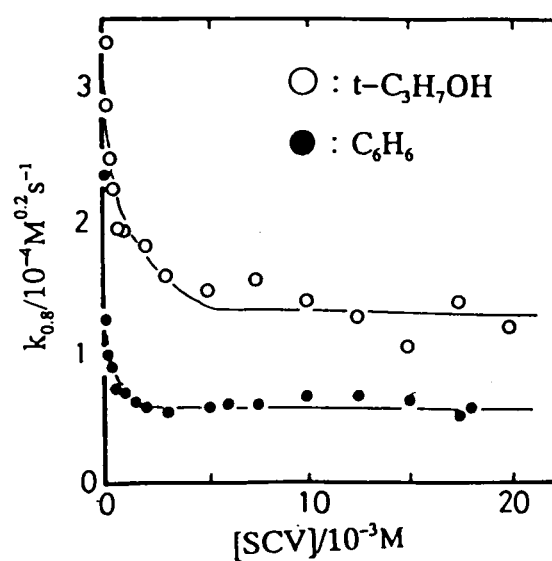


Fig. 2 Effects of free-radical scavenger concentrations on 0.8th order rate constant,  $k_{0.8}$

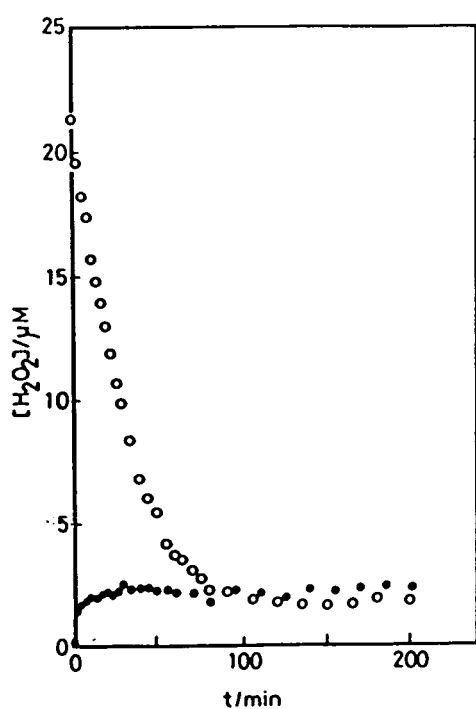


Fig. 3 Time course of hydrogen peroxide concentrations with (○) and without (●) initial hydrogen peroxide. Fe(III) : 20  $\mu$  M.

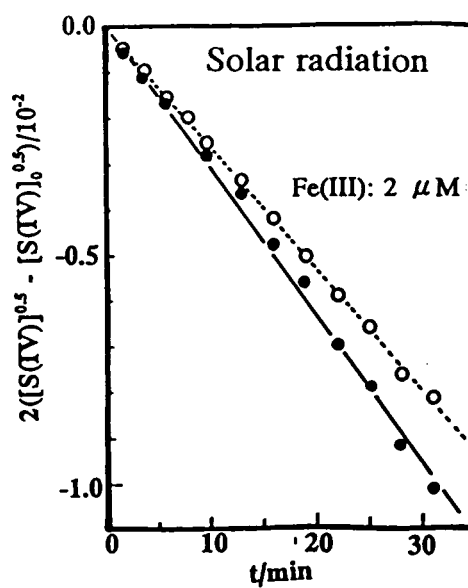


Fig. 4 Photocatalysis with actual solar radiation.