SULPHUR(IV) OXIDATION CATALYSED BY IRON(III) IONS UNDER CONDITIONS REPRESENTATIVE FOR ATMOSPHERIC WATERS

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Abstract

The catalytic S(IV) oxidation in atmospheric water is considered as one of the main reasons for acid rains. The paper presents results of kinetic studies on the S(IV) oxidation catalysed by Fe(III) ions. Laboratory experiments were carried out at concentrations of reactants and pH of solutions representative for acidified atmospheric waters. The results indicate that depending on the initial pH of the reaction solution and Fe(III) ion concentrations, the reaction orders lay in the range 0.5-1.5 and the reaction rates range between $2.10 \cdot 10^{-7}$ and $6.69 \cdot 10^{-6}$ $mol \cdot dm^{-3} \cdot s^{-1}$. The results obtained suggest that the reaction is fast and it may play a significant role in the total oxidation of S(IV) in the atmosphere in highly polluted areas.

Streszczenie

Katalityczne utlenianie S(IV) w wodzie atmosferycznej uważane jest za jedną z głównych przyczyn kwaśnych deszczów. W artykule przedstawiono wyniki badań nad kinetyką procesu utleniania S(IV) katalizowanego jonami Fe(III). Badania laboratoryjne przeprowadzono przy stężeniach reagentów i pH roztworu odpowiadających zakwaszonej wodzie atmosferycznej. Otrzymane wyniki wskazują, że w zależności od początkowego pH roztworu i stężenia jonów Fe(III) rząd reakcji zmienia się w zakresie od 0.5 do 1.5, a szybkości reakcji przyjmują wartości z zakresu $2.10 \cdot 10^{-7}$ – $6.69 \cdot 10^{-6}$ $mol \cdot dm^{-3} \cdot s^{-1}$. Otrzymane wyniki sugerują, że badana reakcja zachodzi szybko i może ona odgrywać znaczącą rolę w całkowitym utlenianiu S(IV) w atmosferze na obszarach silnie zanieczyszczonych.

Keywords: Atmospheric chemistry; Atmospheric waters; S(IV) oxidation; Iron; Catalysis.

1. INTRODUCTION

Atmospheric transformations of sulphur and nitrogen oxides into sulphuric and nitric acids are mainly responsible for acid deposition, which is one of the serious global problems. To develop an effective strategy for reducing this phenomenon, a thorough understanding of the processes leading to its formation is necessary. The formation of H_2SO_4 from SO_2 may take place both in the gas and aqueous phases, but it occurs largely in the aqueous phase, that is in cloud, fog, rain and wet aerosols [1]. The major oxidants in atmospheric waters are O_3, H_2O_2 and O_2. Oxidation by O_2 may be important in the presence of catalysts such as transition metal ions, which are common constituents of atmospheric waters [2-4]. Among transition metal ions, Fe(III) and Mn(II) ions are the most important catalysts in atmospheric droplets, and the catalysed pathway is regarded as a significant contributor to the total oxidation of sulphur dioxide in continental clouds and fogs, in particular in regions where the air is highly polluted, humidity is high and photochemical processes less important [5-10].

Iron is the most abundant transition metal in atmospheric liquid phases (wet aerosol, cloud, fog, rain). The only source of this metal in the atmospheric aque-

ous phase is the dissolution of aerosol particles incorporated in water droplets. The common particles containing iron are soil dust, fly ash from power plants, and exhaust from combustion engines and industrial operations.

Field measurements indicate that the concentration of Fe may vary by several orders magnitude, i.e., between nanomolar and micromolar in rain and between micromolar and millimolar in fogwater [11-13].

The catalysed S(IV) oxidation is complex in both kinetics and mechanism, which has resulted in large discrepancy in both reported kinetic data and in proposed mechanisms. It is a free radical chain reaction which is so sensitive to the reaction conditions that even a slight change in them can cause a change of the dominant path of the reaction course, and thus lead to diverse results. Thus, despite numerous studies on metal ion catalysed S(IV) oxidation more work in this area is needed. Especially there is a lack of information about this process under conditions of highly polluted air where catalytic S(IV) oxidation may play a significant role in the total S(IV) oxidation.

The purpose of the present work was to study the Fe(III)-catalysed S(IV) oxidation under the conditions representative for acidified atmospheric water in heavily polluted areas.

2. MATERIALS AND METHODS

All chemicals used in this study were of analytical grade (Merck). Milli-Q water was used for preparation of all solutions. Stock solutions of Fe(III) were prepared from $Fe_2(SO_4)_3 \cdot nH_2O$. The S(IV) solutions were prepared freshly before each run by dissolving Na_2SO_3 in water which was deoxygenated by bubbling high purity argon through the Milli-Q water for at least 30 min. The initial pH of the solutions was adjusted with H_2SO_4. The source of oxygen for oxi-

dation of S(IV) was synthetic air.

Kinetic experiments were conducted in a 500 cm³ glass cylindrical reactor with four inlet connectors for: pH electrode, introducing reagents, thermometer and teflon tube for sample sipping. The reactor was filled with 450 cm³ of the S(IV) solution acidified to the required pH. The reactor was protected from light and immersed into a thermostat to maintain a constant temperature of 25 ± 1°C. The air was introduced at the bottom of reactor through a ceramal at a rate of 100 ± 2 dm³·h⁻¹. Under these conditions the gas and liquid phases were well mixed and the reaction took place in the kinetic regime, i.e. the global rate of the S(IV) oxidation was limited by the rate of the chemical reaction, not by the diffusion.

To start the reaction, the air flow was turned on and just after that the Mn(II) solution was injected into the reactor. At selected time intervals the concentration of S(IV) was measured by UV-VIS (Shimadzu, Model UV-2101 PC) spectrophotometer equipped with Sipper 260 (Model L) – using flow cell method. The sipping time was set to 5 s, and the slit width was set to 2.0 nm. The S(IV) measurements were carried out at wave lengths 203 nm for the initial pH 3.5 and 205 nm for the initial pH 4.0, 5.0 and 6.0. The pH measurements were performed by an Orion pH meter (Model 710A) combined with a glass electrode. The concentration of Fe(III) was determined by AVANTA PM atomic absorption spectrometer of the GBC.

The experiments were performed under the following conditions: $[S(IV)] \approx 1\cdot10^{-3}$ mol·dm⁻³, $1\cdot10^{-6} \leq [Fe(III)] \leq 1\cdot10^{-5}$ mol·dm⁻³, $3.5 \leq$ the initial pH ≤ 6.0, T = 25°C.

3. RESULTS AND DISCUSSION

Some typical results of the kinetic measurements are shown in Figure 1 as the time dependence of $[S(IV)]_t/[S(IV)]_0$ ratios, where $[S(IV)]_t$ is the concen-

Table 1.
Reaction orders *n* with respect to S(IV) concentration and observed rate constants k_{obs}

Initial pH	[Fe] ≈1·10⁻⁶ mol·dm⁻³		[Fe] ≈5·10⁻⁶ mol·dm⁻³		[Fe] ≈1·10⁻⁵ mol·dm⁻³	
	n	k_{obs} $(mol\cdot dm^{-3})^{(1-n)}\cdot s^{-1}$	n	k_{obs} $(mol\cdot dm^{-3})^{(1-n)}\cdot s^{-1}$	n	k_{obs} $(mol\cdot dm^{-3})^{(1-n)}\cdot s^{-1}$
3.5	0.5	$6.634\cdot10^{-6}$	0.5	$6.610\cdot10^{-5}$	0.5	$1.369\cdot10^{-4}$
4.0	0.5	$1.039\cdot10^{-5}$	1.0	$2.992\cdot10^{-3}$	0.65	$5.086\cdot10^{-4}$
5.0	0.5	$7.645\cdot10^{-6}$	0.5	$5.595\cdot10^{-5}$	0.5	$1.444\cdot10^{-4}$
6.0	1.5	$3.461\cdot10^{-2}$	1.0	$5.784\cdot10^{-3}$	1.0	$6.685\cdot10^{-3}$

Table 2.

Rates of the Fe(III) catalysed S(IV) oxidation at [S(IV)] = $1 \cdot 10^{-3}$ mol·dm^{-3} and at different initial pH values and Fe(III) concentrations

Initial pH	r, (mol·dm^{-3})·s^{-1}		
	[Fe] $\approx 1 \cdot 10^{-6}$ mol·dm^{-3}	[Fe] $\approx 5 \cdot 10^{-6}$ mol·dm^{-3}	[Fe] $\approx 1 \cdot 10^{-5}$ mol·dm^{-3}
3.5	$2.098 \cdot 10^{-7}$	$2.090 \cdot 10^{-6}$	$4.329 \cdot 10^{-6}$
4.0	$3.286 \cdot 10^{-7}$	$2.992 \cdot 10^{-6}$	$5.707 \cdot 10^{-6}$
5.0	$2.417 \cdot 10^{-7}$	$1.769 \cdot 10^{-6}$	$4.565 \cdot 10^{-6}$
6.0	$1.094 \cdot 10^{-7}$	$5.783 \cdot 10^{-6}$	$6.685 \cdot 10^{-6}$

tration of S(IV) at time t, and $[S(IV)]_0$ is the initial concentration of S(IV). Based on the measurement results, the kinetic law parameters for the processes studied were determined.

The rate of Fe(III)-catalysed S(IV) oxidation has been described by the equation:

$$r = -\frac{d[S(IV)]}{dt} = k_{obs}[S(IV)]^n \qquad (1)$$

where k_{obs} is the observed rate constant, and n is the reaction order with respect to S(IV) concentration.

The reaction orders and rate constants determined by the standard integral technique are listed in Table 1. The S(IV) oxidation catalysed by Fe(III) ions is 0.5 order with respect to S(IV) concentration ($n = 0.5$) at initial pH values 3.5 and 5.0 over the entire studied range of Fe(III) concentrations. At the initial pH 4.0 the reaction order is 0.5 only at the lowest Fe(III) concentration ($1 \cdot 10^{-6}$ mol·dm^{-3}), and at the higher Fe(III) concentrations ($5 \cdot 10^{-6}$ and $1 \cdot 10^{-5}$ mol·dm^{-3}) the reaction order is higher than 0.5. At an initial pH of 6.0 the reaction order with respect to S(IV) concentration is 1 at higher Fe(III) concentrations and it is 1.5 at the lowest Fe(III) concentration.

The S(IV) oxidation rates are given in Table 2. The results show that the oxidation rate is dependent both on the Fe(III) concentration and on the initial pH of the solution.

The influence of the Fe(III) concentration on the reaction rate is larger than the influence of the initial pH. In the initial pH range from 3.5 to 5.0 the reaction rate increases about 17-20 times with increasing the Fe(III) concentration from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-5}$ mol·dm^{-3}, and at pH 6 the rate increases about 6 times. The oxidation at Fe(III) concentrations of $5 \cdot 10^{-6}$ and $1 \cdot 10^{-5}$ mol·dm^{-3} is very fast. About 90% of S(IV) is oxidized after 5-15 minutes (Fig. 1b, 1c).

A change in the initial pH from 3.5 to 6.0 leads only
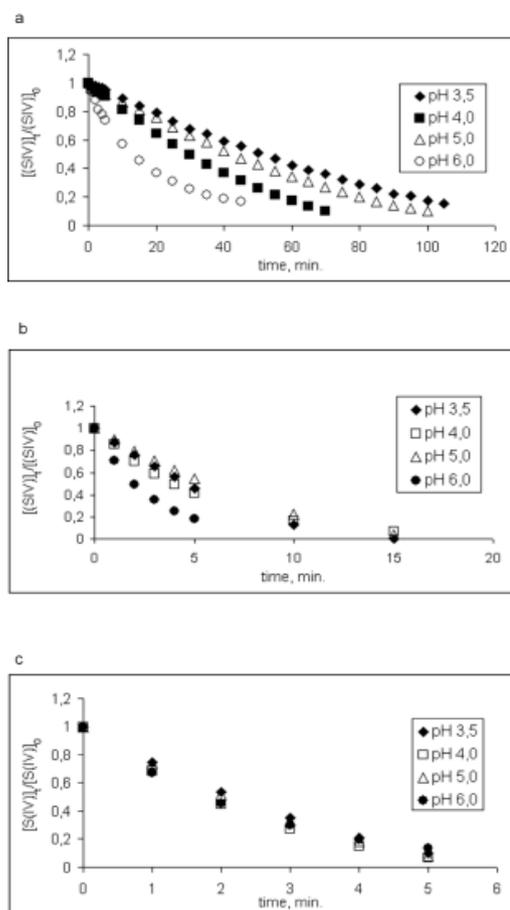
Figure 1.
The ratio of S(IV) concentration at time t to the initial S(IV) concentration as a function of time for the Fe(III)-catalysed S(IV) oxidation.
a – [Fe(III)] = $1 \cdot 10^{-6}$ mol·dm^{-3}
b – [Fe(III)] = $5 \cdot 10^{-6}$ mol·dm^{-3}
c – [Fe(III)] = $1 \cdot 10^{-5}$ mol·dm^{-3}

to 1.5-5 fold increase in the oxidation rate depending on the Fe(III) concentration. The influence of the initial pH decreases with increase in the Fe(III) concentration. At Fe(III) concentration of $1 \cdot 10^{-5}$ mol·dm^{-3} the effect of the initial pH is slight (Fig. 1c).

The strongest influence of the initial pH is observed at the lowest Fe(III) concentration ($1 \cdot 10^{-6}$ mol·dm^{-3}). The observed initial pH dependence is somewhat complex. An increase in the initial pH from 3.5 to 4.0 results in a rise in the oxidation rate, but an increase in the initial pH from 4.0 to 5.0 leads to a decrease in the oxidation rate, and then the oxidation rate begins to increase with increasing the initial pH above pH 5.0. There are two reasons for this dependence: firstly, solubility of iron hydroxides decreases above pH 4.0 leading to decrease in concentration of Fe(III) ions, which are actual catalyst, secondly, above pH 5.0 the non-catalytic S(IV) oxidation rate significantly increases. Therefore, the S(IV) oxidation may be faster at pH 6.0 than at pH 5.0 even though the concentration of Fe(III) ions is lower.

4. CONCLUSIONS

1. The reaction order with respect to the S(IV) concentration varies from 0.5 to 1.5 depending on the Fe(III) concentration and the initial pH.

2. The S(IV) oxidation rate depends both on the Fe(III) concentration and on the initial pH of the solution. The influence of the Fe(III) concentration on the reaction rate is larger than the influence of the initial pH. At the Fe(III) concentration $1 \cdot 10^{-5}$ mol·dm^{-3} the reaction proceeds 6-20 times faster than at the Fe(III) concentration $1 \cdot 10^{-6}$ mol·dm^{-3}, whereas a change in the initial pH from 3.5 to 6.0 causes only about 1.5-5-fold increase in the reaction rate.

3. At higher Fe(III) concentrations ($5 \cdot 10^{-6}$ and $1 \cdot 10^{-5}$ mol·dm^{-3}) the reaction proceeds very fast. After short time (5 minutes for the Fe(III) concentration $5 \cdot 10^{-6}$ mol·dm^{-3} and 15 minutes for the Fe(III) concentration $1 \cdot 10^{-5}$ mol·dm^{-3}) about 90% of S(IV) is already oxidized.

4. The results obtained indicate that the Fe(III) catalysed S(IV) oxidation may play a significant role in the total oxidation of S(IV) in the atmosphere in highly polluted areas.

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