SULPHUR(IV) OXIDATION BY OXYGEN IN THE PRESENCE OF COBALT(II) IONS IN ATMOSPHERIC WATERS

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Abstract

The paper presents results of study on catalytic effect of Co(II) ions on the oxidation of S(IV) in aqueous solutions. Laboratory experiments were carried out at concentrations of reactants and pH found in atmospheric waters in heavily polluted atmospheres. The kinetic law parameters, i.e. the observed rate constant and the reaction order with respect to S(IV) concentration, were determined. Depending on the initial pH of the reaction solution and Co(II) ion concentrations the S(IV) oxidation rates range between $2.2 \cdot 10^{-8}$-$1.6 \cdot 10^{-5}$ mol$\cdot$dm$^{-3} \cdot$s^{-1}. The results obtained show that at an initial pH of 3.5- 5.0 catalytic activity of Co(II) is slight and it becomes significant at an initial pH of 6.0.

Streszczenie

W artykule przedstawiono wyniki badań nad katalitycznym działaniem jonów Co(II) na utlenianie S(IV) w roztworach wodnych. Badania laboratoryjne przeprowadzono przy stężeniach reagentów i pH roztworu spotykanych w wodach atmosferycznych na obszarach silnie zanieczyszczonych. Wyznaczono parametry równań kinetycznych tj. obserwowane stałe szybkości i rząd reakcji względem stężenia S(IV). W zależności od początkowego pH roztworu i stężeń jonów kobaltu szybkość reakcji utleniania zmieniała się w zakresie $2.2 \cdot 10^{-8}$-$1.6 \cdot 10^{-5}$ mol$\cdot$dm$^{-3} \cdot$s^{-1}. Otrzymane wyniki wskazują, że przy początkowym pH roztworu w zakresie 3.5-5.0 aktywność katalityczna jonów Co(II) jest nieznaczna, staje się ona znacząca dopiero przy początkowym pH 6.0.

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

1. INTRODUCTION

Emitted into the atmosphere sulphur dioxide can be directly removed through dry or wet deposition. The main sink of atmospheric SO_2, however, is the oxidation to sulphate(VI) occurring both in the gas phase and in the liquid phase of wet aerosols, clouds, fogs and rain. These processes are important for the generation of acid rain.

Sulphur (IV) oxidation reactions occur at a much faster rate in the liquid phase than in the gas phase [1].

The major oxidants in atmospheric waters are O_3, H_2O_2 and O_2. Aqueous phase SO_2 oxidation by molecular oxygen is only important in the presence of transition metal ions as catalysts.

Transition metals are chemically defined as elements that form at least one ion with a partially filled "d" sublevel orbital. These elements therefore have several oxidation states that allow them to catalyse chemical reactions and form complexes. Transition metals are ubiquitous in atmospheric liquid phases (wet aerosol, cloud, fog, rain). The source of these metals is

the dissolution of the soluble fraction of atmospheric aerosols in the aqueous phase.

Cobalt is found in soil, dust, seawater, volcanic emissions, and smoke from forest and bush fires. Cobalt is mainly emitted from sources where it is used in the production of steel and other alloys. Automotive repair shops may be significant emitters of cobalt. It will also be emitted to air during the mining or refining of nickel, copper, silver, lead and iron. Small amounts of cobalt have been found in motor vehicle exhaust.

At unpolluted sites, mean cobalt levels are typically < 1-2 ng/m^3 [2, 3]. In urban and industrialized areas the ambient air concentration of cobalt is usually higher, it is reported to range from less than 1 to 2 ng/m^3 up to 10 ng/m^3 near industrial sources and exceeding 10 ng/m^3 in heavily industrialized cities. Seiler et al. [4] reported the cobalt concentrations in ambient air in several places in North and South America and in the United Kingdom and found that the levels were in the range 0.07 ng/m^3 to 5 ng/m^3. Near a nickel refinery in Wales the average atmospheric cobalt concentration was recorded at 48 ng/m^3 [2]. In one industrial area in the United States, levels of 610 ng/m^3 were measured [5].

Many in situ measurements underscore significant concentrations of transition metals in the various atmospheric aqueous phases. The concentration of iron may vary by several orders magnitude, i.e., between nanomolar and micromolar in rain and between micromolar and millimolar in fogwater. Concentrations of other transition metals are generally between 10 and 100 times lower than those of iron [6-10].

In rainwater, mean cobalt concentrations are between 0.3 μg/dm^3 in rural areas and 1.7 μg/dm^3 in highly industrial areas [11, 12]. The highest recorded concentration was 68.9 μg/dm^3 in the vicinity of a nickel smelter at Monchegorsk in the Russian Arctic [13].

Transition metal concentrations in fog- and cloudwater are about 10 times higher than those in rainwater and in wet aerosols they are 100 times higher [14].

The catalysed S(IV) oxidation by O$_2$ in the aqueous phase may contribute significantly to the total oxidation of sulphur dioxide in continental clouds and fogs, in particular in regions where humidity is high and the air is highly polluted.

The Fe- and Mn-catalysed aqueous S(IV) oxidation by oxygen has been extensively investigated [15-18]. Nevertheless, the complexity of this free radical chain reaction has resulted in significant discrepancies in the reported kinetic data and in the proposed mechanisms. Some studies on catalysis of S(IV) oxidation by other transition metals: copper [15, 19], cobalt [20, 21], chromium, and vanadium [22, 23] have also been performed but these processes are still far from being fully elucidated and more work in this area is indicated.

In this work we investigated the effect of Co(II) on the oxidation of S(IV) by oxygen in the aqueous phase under conditions representative for 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 Co(II) were prepared from CoSO$_4$·7H$_2$O. The S(IV) solutions were prepared freshly before each run by dissolving Na$_2$SO$_3$ 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$_2$SO$_4$. The source of oxygen for oxidation of S(IV) was synthetic air.

Kinetic experiments were conducted in a 500 cm^3 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 cm^3 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 dm^3·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 Co(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 concen-

tration of Co(II) was determined by AVANTA PM atomic absorption spectrometer of the GBC.

The experiments were performed under the following conditions: $[S(IV)] \approx 1 \cdot 10^{-3}$ mol·dm^{-3}, $1 \cdot 10^{-6} \leq [Co(II)] \leq 1 \cdot 10^{-5}$ mol·dm^{-3}, $3.5 \leq$ the initial pH ≤ 6.0, T = 25°C.

3. RESULTS AND DISCUSSION

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 concentration of S(IV) at time t, and $[S(IV)]_0$ is the initial concentration of S(IV). At initial pH values in the range of 3.5-5.0 the reaction is very slow. Under these conditions only 17-30% S(IV) is oxidised after 200 minutes. At an initial pH of 6.0 the reaction proceeds faster and degree of S(IV) oxidation is about 50-65% after 200 minutes.

Based on the measurement results, the kinetic law parameters for the processes studied were determined. The rate of Co(II)-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 reaction order n with respect to S(IV) concentration varies from 2.5 to 10.0 depending on the initial pH and Co(II) concentration.

The Co(II) catalysed S(IV) oxidation rates are given in Table 2. At low initial pH values (3.5-5.0) the oxidation rate is small ($1.1 \cdot 10^{-8}$-$1.0 \cdot 10^{-7}$ mol·dm^{-3}·s^{-1}). At an initial pH of 6.0 it increases to $5.5 \cdot 10^{-6}$ mol·dm^{-3}·s^{-1} at Co(II) concentration of $1 \cdot 10^{-6}$ mol·dm^{-3} and to $2.1 \cdot 10^{-5}$ mol·dm^{-3}·s^{-1} at Co(II) concentration of $1 \cdot 10^{-5}$ mol·dm^{-3}.

To assessment catalytic activity of Co(II) the noncatalytic S(IV) oxidation rate under the same conditions were also determined. The results are presented in Table 3. Over initial pH values of 3.5 to 5.0 the noncatalytic oxidation rate is very small and it lies in the range $1.3 \cdot 10^{-8}$-$1.7 \cdot 10^{-8}$ mol·dm^{-3}·s^{-1}, but at an initial pH of 6.0 it is an order of magnitude greater.

Ratios of the Co(II) catalysed oxidation rate to the noncatalytic oxidation rate are listed in Table 4. We can see that Co(II) has significant catalytic activity at
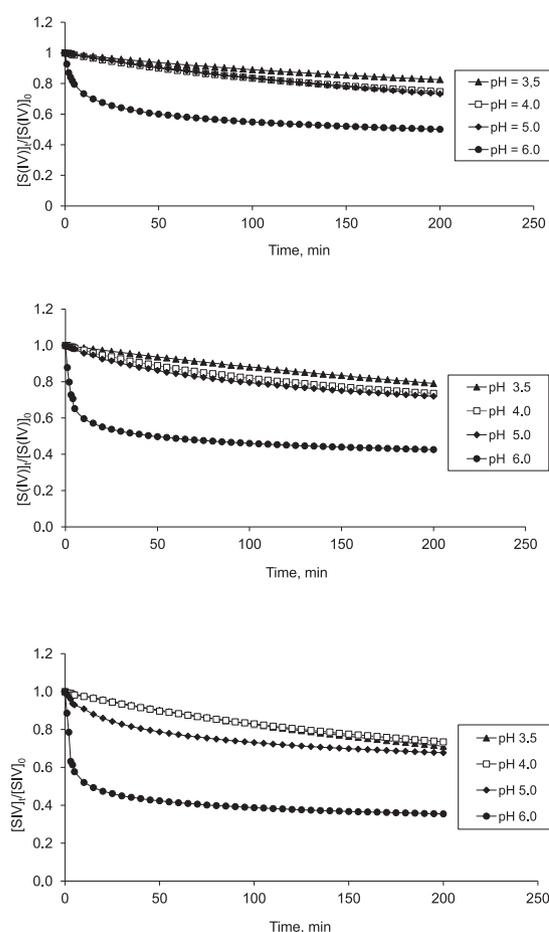
Figure 1.
The ratio of S(IV) concentration at time t to the initial S(IV) concentration as a function of time for the Co(II)-catalysed S(IV) oxidation.
a – $[Co(II)] = 1 \cdot 10^{-6}$ mol·dm^{-3}
b – $[Co(II)] = 5 \cdot 10^{-6}$ mol·dm^{-3}
c – $[Co(II)] = 1 \cdot 10^{-5}$ mol·dm^{-3}

an initial pH of 6.0. Depending on the Co(II) concentration the S(IV) oxidation rate is 36.7 to 143.6 times greater than that of the noncatalytic oxidation. At lower initial pH values the catalytic action of Co(II) is small in the entire range of Co(II) concentrations studied. Concentrations of Co(II) in solutions used in our experiments correspond to those found in wet aerosols in highly industrial areas and also in clouds and fogs near industrial sources.

It is difficult to make a direct comparison between the present results and the few reported in the literature because of different experimental conditions or considering other aspect of the process. Zhao et al. [20] made a study on the reaction rate of sulphite oxidation with cobalt ion catalyst but at experimental condi-

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

Initial pH	[Co] $\approx 1 \cdot 10^{-6}$ mol·dm^{-3}		[Co] $\approx 5 \cdot 10^{-6}$ mol·dm^{-3}		[Co] $\approx 1 \cdot 10^{-5}$ mol·dm^{-3}	
	n	k_{obs} (mol·dm^{-3})$^{(1-n)}$·s^{-1}	n	k_{obs} (mol·dm^{-3})$^{(1-n)}$·s^{-1}	n	k_{obs} (mol·dm^{-3})$^{(1-n)}$·s^{-1}
3.5	5.5	$3.627 \cdot 10^{8}$	2.5	0.712	2.5	1.043
4.0	4.5	$9.188 \cdot 10^{5}$	5.0	$3.155 \cdot 10^{7}$	4.0	$2.955 \cdot 10^{4}$
5.0	3.0	$2.509 \cdot 10^{1}$	6.5	$2.069 \cdot 10^{12}$	9.5	$3.286 \cdot 10^{21}$
6.0	6.5	$1.726 \cdot 10^{20}$	9.0	$1.599 \cdot 10^{22}$	10.0	$2.136 \cdot 10^{25}$

Table 2.
The Co(II)-catalysed S(IV) oxidation rate (r_{Co}) at [S(IV)] = $1 \cdot 10^{-3}$ mol·dm^{-3} and at different initial pH values and Co(II) concentrations

Initial pH	r_{Co}, mol·dm^{-3}·s^{-1}		
	[Co] $\approx 1 \cdot 10^{-6}$ mol·dm^{-3}	[Co] $\approx 5 \cdot 10^{-6}$ mol·dm^{-3}	[Co] $\approx 1 \cdot 10^{-5}$ mol·dm^{-3}
3.5	$1.147 \cdot 10^{-8}$	$2.251 \cdot 10^{-8}$	$3.299 \cdot 10^{-8}$
4.0	$2.905 \cdot 10^{-8}$	$3.155 \cdot 10^{-8}$	$2.955 \cdot 10^{-8}$
5.0	$2.509 \cdot 10^{-8}$	$6.543 \cdot 10^{-8}$	$1.039 \cdot 10^{-7}$
6.0	$5.458 \cdot 10^{-8}$	$1.599 \cdot 10^{-8}$	$2.136 \cdot 10^{-5}$

Table 3.
Reaction order n with respect to S(IV) concentration, observed rate constant k_{obs} and reaction rate (r_n) at [S(IV)] = $1 \cdot 10^{-3}$ mol·dm^{-3} for the noncatalytic S(IV) oxidation

Initial pH	n	k_{obs} (mol·dm^{-3})$^{(1-n)}$·s^{-1}	r_n (mol·dm^{-3})$^{(1-n)}$·s^{-1}
3.5	0	$1.327 \cdot 10^{-8}$	$1.327 \cdot 10^{-8}$
4.0	0	$1.288 \cdot 10^{-8}$	$1.288 \cdot 10^{-8}$
5.0	0	$1.722 \cdot 10^{-8}$	$1.722 \cdot 10^{-8}$
6.0	2	$1.487 \cdot 10^{-1}$	$1.487 \cdot 10^{-7}$

Table 4.
Ratio of the noncatalytic to the Co(II)-catalysed S(IV) oxidation rate

Initial pH	r_{Co}/r_n		
	[Co] $\approx 1 \cdot 10^{-6}$ mol·dm^{-3}	[Co] $\approx 5 \cdot 10^{-6}$ mol·dm^{-3}	[Co] $\approx 1 \cdot 10^{-5}$ mol·dm^{-3}
3.5	0.86	1.69	2.48
4.0	2.25	2.50	2.29
5.0	1.46	3.80	6.03
6.0	36.7	107.5	143.6

tions representative for flue gas desulphurization rather than for the process in atmospheric waters. Pasiuk-Bronikowska et al. [21] investigated the reaction under conditions relevant to atmospheric waters but their study was concerned to the mechanism of the reaction. However, they also observed significant catalytic activity of Co(II) ions at higher pH values.

4. CONCLUSIONS

1. The catalytic activity of Co(II) depends primarily on the initial pH of the solution. At low initial pH values (< 5.0) catalytic activity of Co(II) is negligible; it is significant only at higher initial pH values.

2. At higher initial pH values the S(IV) oxidation rate also depends on the Co(II) concentration. At an initial pH of 6.0 the S(IV) oxidation rate at Co(II) concentration of $1 \cdot 10^{-5}$ mol·dm^{-3} is about 4 times higher than at that of $1 \cdot 10^{-6}$ mol·dm^{-3}.

3. The results obtained indicate that the Co(II) catalysed S(IV) oxidation may play a significant role in the total oxidation of S(IV) in the atmosphere only in highly industrial areas and near industrial sources when pH of atmospheric waters is above 5.

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