

Irena WILKOSZ¹ and Dorota SMALCERZ

**SULPHUR(IV) OXIDATION
CATALYSED BY MANGANESE(II) IONS
UNDER CONDITIONS REPRESENTATIVE
FOR ATMOSPHERIC WATERS**

**UTLENIANIE SIARKI(IV) KATALIZOWANE JONAMI MANGANU(II)
W WARUNKACH REPREZENTATYWNYCH
DLA WÓD ATMOSFERYCZNYCH**

Abstract: Results of kinetic studies on the S(IV) oxidation catalysed by Mn(II) ions were presented. Laboratory experiments were carried out at concentrations of reactants and pH of solutions representative for acidified atmospheric waters. The results indicate that at an initial pH of the reaction solution from 3.5 to 5.0 the reaction rate is independent of S(IV) concentration i.e., the reaction is zero order with respect to S(IV) concentration ($n = 0$). At an initial pH of 6.0 the reaction order n changes with the reaction time. At the beginning of the process $n \neq 0$, and then it changes into 0. The S(IV) oxidation rate depends on both Mn(II) concentration and initial pH of the solution. Under studied conditions 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.

Keywords: atmospheric chemistry, atmospheric waters, S(IV) oxidation, manganese, catalysis

One of the important atmospheric processes leading to the formation of acidic precipitation is the catalytic oxidation of S(IV) species by oxygen in atmospheric water droplets. It has been known that some transition metal ions are able to catalyse this process [1]. The most efficient catalysts are iron(II/III) and manganese(II/III). These metals are common constituents of tropospheric aerosols in heavy polluted urban and industrial areas. The common particles containing trace metals are soil dust, fly ash from power plants, and exhaust from combustion engines and industrial operations.

The only source of these metals in the atmospheric aqueous phase is the dissolution of aerosol particles incorporated in water droplets. Concentrations of Mn(II) dissolved in atmospheric waters in urban and industrial areas range from 10^{-7} to 10^{-6} mol/dm³ in rain [2], and from 10^{-6} to 10^{-5} mol/dm³ in fog and cloudwater [1, 3].

¹ Department of Air Protection, Silesian University of Technology, ul. Akademicka 2, 44-100 Gliwice, Poland, phone: +48 032 237 1519, fax: +48 032 237 1290, email: Irena.Wilkosz@polsl.pl

The catalysed S(IV) oxidation is regarded as a significant process in the total oxidation of sulphur dioxide in continental clouds and fogs, in particular in regions where the air is highly polluted. This process is the subject of a number of studies [eg 4–15].

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 Mn(II)-catalysed S(IV) oxidation under the conditions representative for acidified atmospheric water in heavily polluted areas.

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 Mn(II) were prepared from $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. 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 oxidation 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 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. Under these conditions the gas and liquid phases were well mixed and the reaction took place in the kinetic regime, ie the global rate of the S(IV) oxidation was limited by the rate of 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 wavelengths $\lambda = 203$ nm for the initial pH 3.5 and $\lambda = 205$ 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 Mn(II) was determined by AVANTA PM atomic absorption spectrometer of the GBC.

The experiments were performed under the following conditions: $[\text{S(IV)}] \approx 1 \cdot 10^{-3}$ mol/dm³, $1 \cdot 10^{-6} \leq [\text{Mn(II)}] \leq 1 \cdot 10^{-5}$ mol/dm³, $3.5 \leq$ the initial pH ≤ 6.0 , $T = 25$ °C.

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 concentration 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.

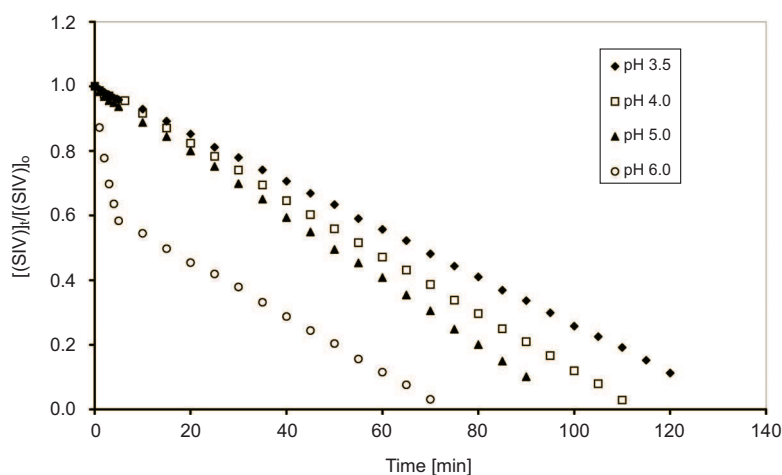


Fig. 1. Effect of initial pH values on the Mn(II)-catalysed S(IV) oxidation. $[S(IV)]_0 = 1 \cdot 10^{-3} \text{ mol/dm}^3$, $[Mn(II)] = 5 \cdot 10^{-6} \text{ mol/dm}^3$

Since the rate of Mn(II)-catalysed S(IV) oxidation is independent of oxygen concentration [16, 17], the reaction rate has been described by the equation:

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

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 Tables 1–2. The S(IV) oxidation catalysed by Mn(II) ions is zero order with respect to S(IV) concentration ($n = 0$) over the entire studied range of Mn(II) concentrations and at initial pH values in the range of 3.5–5.0. At an initial pH of 6.0 the reaction order with respect to S(IV) concentration changes with the reaction time. At the beginning it is different from 0 and then it changes into 0. At $[Mn(II)] \approx 1 \cdot 10^{-6} \text{ mol/dm}^3$ $n = 3$ from 0 to 1800 s, and then it changes into 0. At higher Mn(II) concentrations ($5 \cdot 10^{-6}$ and $1 \cdot 10^{-5} \text{ mol/dm}^3$) $n = 2$ at the beginning of the process and after 300 s it changes into 0, that is, into such order as for lower pH. This change in the reaction order n can be explained by an influence of the initial pH on the S(IV) oxidation rate. The results (Table 1) show that a change in the initial pH from 3.5 to 5.0 gives rather small increase in the oxidation rate whereas the change in the initial pH

from 5.0 to 6.0 causes considerably greater increase in the reaction rate. At an initial pH of 6.0 the oxidation proceeds very fast and in consequence pH of the reaction solution decreases rapidly, which causes both a decrease in the oxidation rate and a change in the reaction order.

Table 1

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

Initial pH	$[\text{Mn}] \approx 1 \cdot 10^{-6} \text{ mol/dm}^3$		$[\text{Mn}] \approx 5 \cdot 10^{-6} \text{ mol/dm}^3$		$[\text{Mn}] \approx 1 \cdot 10^{-5} \text{ mol/dm}^3$	
	n	$k_{\text{obs}} (\text{mol/dm}^3)^{1-n} \cdot \text{s}^{-1}$	n	$k_{\text{obs}} (\text{mol/dm}^3)^{1-n} \cdot \text{s}^{-1}$	n	$k_{\text{obs}} (\text{mol/dm}^3)^{1-n} \cdot \text{s}^{-1}$
3.5	0	$4.023 \cdot 10^{-8}$	0	$1.446 \cdot 10^{-7}$	0	$4.894 \cdot 10^{-7}$
4.0	0	$4.845 \cdot 10^{-8}$	0	$1.739 \cdot 10^{-7}$	0	$5.520 \cdot 10^{-7}$
5.0	0	$5.903 \cdot 10^{-8}$	0	$1.970 \cdot 10^{-7}$	0	$8.263 \cdot 10^{-7}$
6.0	3.0 (0–1800 s)	$6.097 \cdot 10^2$ (0–1800 s)	2.0 (0–300 s)	2.403 (0–300 s)	2.0 (0–300 s)	2.703 (0–300 s)
	0 (> 1800 s)	$2.427 \cdot 10^{-8}$ (> 1800 s)	0 (> 300 s)	$1.412 \cdot 10^{-7}$ (> 300 s)	0 (> 300 s)	$3.678 \cdot 10^{-7}$ (> 300 s)

The oxidation rate r is equal to k_{obs} if $n = 0$, and $r = k_{\text{obs}}[\text{S(IV)}]^n$ if $n \neq 0$. The value of the oxidation rate is dependent on Mn(II) concentration and initial pH of the solution (Table 2).

Table 2

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

Initial pH	$r (\text{mol/dm}^3) \cdot \text{s}^{-1}$		
	$[\text{Mn}] \approx 1 \cdot 10^{-6} \text{ mol/dm}^3$	$[\text{Mn}] \approx 5 \cdot 10^{-6} \text{ mol/dm}^3$	$[\text{Mn}] \approx 1 \cdot 10^{-5} \text{ mol/dm}^3$
3.5	$4.023 \cdot 10^{-8}$	$1.446 \cdot 10^{-7}$	$4.894 \cdot 10^{-7}$
4.0	$4.845 \cdot 10^{-8}$	$1.739 \cdot 10^{-7}$	$5.520 \cdot 10^{-7}$
5.0	$5.903 \cdot 10^{-8}$	$1.970 \cdot 10^{-7}$	$8.263 \cdot 10^{-7}$
6.0	$6.097 \cdot 10^{-7}$ (0–1800 s)	$2.403 \cdot 10^{-6}$ (0–300 s)	$2.703 \cdot 10^{-6}$ (0–300 s)
	$2.427 \cdot 10^{-8}$ (> 1800 s)	$1.412 \cdot 10^{-7}$ (> 300 s)	$3.678 \cdot 10^{-7}$ (> 300 s)

In the initial pH range from 3.5 to 5.0 the influence of Mn(II) concentration on the reaction rate is larger than the influence of the initial pH. The reaction rate increases about 11–14 times with increasing Mn(II) concentration from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-5} \text{ mol/dm}^3$, whereas the change in the initial pH from 3.5 to 5.0 causes only 1.4–1.7 fold increase in the oxidation rate.

At initial pH values in the range of 5.0–6.0 the situation is different. The change in the initial pH from 5.0 to 6.0 leads to significant increase in the reaction rate (from several to a dozen or so times depending on Mn(II) concentration), but after short time (1800 s for Mn(II) concentration $1 \cdot 10^{-6}$ mol/dm³, and 300 s for higher Mn(II) concentrations) the reaction rate decreases to the level close to that for the initial pH 3.5.

At low pH range (3.5–5.0) the S(IV) oxidation proceeds at constant rate (at a given Mn(II) concentration). At pH 6.0 the course of the reaction is different, in the beginning the S(IV) oxidation rate is high and it is dependent on S(IV) concentration ($n \neq 0$), and then the S(IV) oxidation rate is smaller and it is independent of [S(IV)] ($n = 0$).

Conclusions

The S(IV) oxidation catalysed by Mn(II) ions is zero order with respect to S(IV) concentration ($n = 0$) over the entire studied range of Mn(II) concentrations ($1 \cdot 10^{-6}$ – $1 \cdot 10^{-5}$ mol/dm³) and at initial pH values in the range of 3.5–5.0. At an initial pH of 6.0 the reaction order n changes with the reaction time. At the beginning of the process $n \neq 0$, and then it changes into 0.

The S(IV) oxidation rate depends on both Mn(II) concentration and initial pH of the solution. In the initial pH range from 3.5 to 5.0 the influence of Mn(II) concentration on the reaction rate is larger than the influence of the initial pH. At Mn(II) concentration $1 \cdot 10^{-5}$ mol/dm³ the reaction proceeds a dozen or so times faster than at Mn(II) concentration $1 \cdot 10^{-6}$ mol/dm³, whereas a change in the initial pH from 3.5 to 5.0 causes only about 1.5-fold increase in the reaction rate. However, an increase in the initial pH above 5.0 causes a rapid increase in the reaction rate. At the initial pH 6.0 the reaction proceeds very fast. After short time (1800 s for Mn(II) concentration $1 \cdot 10^{-6}$ mol/dm³, and 300 s for higher Mn(II) concentrations) about 50 % of S(IV) is already oxidized, and then the reaction rate decreases to the level close to that for the initial pH 3.5.

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

References

- [1] Brandt C. and van Eldik R.: Chem. Rev. 1995, **95**, 119–180.
- [2] Deutsch F., Hoffmann P. and Ortner H.M.: Anal. Bioanal. Chem. 1997, **357**, 105–111.
- [3] Millet M., Wortham H. and Mirabel Ph.: Atmos. Environ. 1995, **29**, 2626–2631.
- [4] Penkett S.A., Jones B.M.R. and Eggleton A.E.J.: Atmos. Environ. 1979, **13**, 139–147.
- [5] Pasiuk-Bronikowska W. and Bronikowski T.: Chem. Eng. Sci. 1981, **36**, 215–219.
- [6] Martin L.R. and Hill M.W.: Atmos. Environ. 1987, **21**, 2267–2270.
- [7] Ibusuki T. and Barnes H.M.: Atmos. Environ. 1984, **18**, 145–151.
- [8] Kraft J. and van Eldik R.: Inorg. Chem. 1989, **28**, 2297–2305.
- [9] Grgić I., Hudnik V., Bizjak M. and Levec J.: Atmos. Environ. 1991, **25A**, 1591–1597.
- [10] Grgić I., Hudnik V., Bizjak M. and Levec, J.: Atmos. Environ. 1992, **26A**, 571–577.
- [11] Berglund J. and Elding L.J.: Atmos. Environ. 1995, **29**, 1379–1391.
- [12] Novič M., Grgić I., Poje M. and Hudnik V.: Atmos. Environ. 1996, **30**, 4191–4196.
- [13] Turšič J., Grgić I. and Podkrajšek B.: Atmos. Environ. 2003, **37**, 2589–2595.

- [14] Ziajka J. and Pasiuk-Bronikowska W.: Atmos. Environ. 2005, **39**, 1431–1438.
[15] Podkrajšek B., Grgić I., Turšič J. and Berčič G.: J. Atmos. Chem. 2006, **54**, 103–120.
[16] Huss A. Jr., Lim P. and Eckert C.: J. Phys. Chem. 1982, **86**, 4229–4233.
[17] Connick R. and Zhang Y.: Inorg. Chem. 1996, **35**, 4613–4621.

**UTLENIANIE SIARKI(IV) KATALIZOWANE JONAMI MANGANU(II)
W ROZTWORACH WODNYCH W WARUNKACH REPREZENTATYWNYCH
DLA WÓD ATMOSFERYCZNYCH**

Katedra Ochrony Powietrza, Politechnika Śląska, Gliwice

Abstrakt: Przedstawiono wyniki badań nad kinetyką utleniania S(IV) katalizowanego jonami Mn(II). Badania laboratoryjne przeprowadzono przy stężeniach reagentów i pH roztworu odpowiadających zakwaszonej wodzie atmosferycznej. Otrzymane wyniki wskazują, że przy początkowym pH roztworu w zakresie od 3,5 do 5,0 szybkość reakcji nie zależy od stężenia S(IV), tj. reakcja jest zerowego rzędu względem stężenia S(IV) ($n = 0$). Przy początkowym pH 6 rząd reakcji n zmienia się z czasem reakcji. Na początku procesu $n \neq 0$, a następnie przyjmuje wartość 0. Szybkość utleniania S(IV) zależy od stężenia Mn(II) i od początkowego pH roztworu. W badanych warunkach reakcja zachodzi szybko i może ona odgrywać znaczącą rolę w całkowitym utlenianiu S(IV) w atmosferze na obszarach silnie zanieczyszczonych.

Słowa kluczowe: chemia atmosfery, wody atmosferyczne, utlenianie S(IV), mangan, kataliza