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Research Paper

Effect of Chromium(III) on the Sulphur(IV) Oxidation Catalysed by Manganese(II) under Conditions Representative for Atmospheric Waters

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Abstract: *The kinetics of the S(IV) oxidation in aqueous solutions in the presence of Cr(III) and Mn(II) ions was studied and the influence of Cr(III) ions on the S(IV) oxidation catalysed by Mn(II) ions was determined. 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 constants and the reaction orders with respect to S(IV) concentration, were determined. The results obtained for the S(IV) oxidation in the presence of Cr(III) ions only, show that Cr(III) ions have little catalytic effect on the S(IV) oxidation. Under conditions studied, this effect was several times smaller than that of Mn(II) ions. The S(IV) oxidation rate in the simultaneous presence of Mn(II) and Cr(III) ions was greater or smaller than that in the presence of Mn(II) ions only, depending on the reaction conditions. However, it was always smaller than expected from the sum of the two individual rates (in the presence of Mn(II) ions alone and in the presence of Cr(III) ions alone), which shows that there is antagonism between Mn(II) and Cr(III) ions. The magnitude of this antagonistic effect depends on an initial pH and concentrations of both Mn(II) and Cr(III) ions. At low values of these parameters, the antagonistic effect is rather small, but at higher values of them, it may be strong.*

Keywords: Atmospheric chemistry, S(IV) oxidation, chromium, manganese, catalysis, antagonism.

Introduction

Sulphur and nitrogen oxides emitted into the atmosphere are oxidized to form sulphuric (H_2SO_4) and nitric (HNO_3) acids, which eventually fall back to the Earth's surface as acid deposition. Sulphur dioxide emission is the most common contributor to acid deposition, responsible for about 70% of the total. Acid deposition is a problem of great importance to society because of acidification of surface waters and subsequent damage to aquatic ecosystems, damage to forests and vegetation, damage of materials and structures. Moreover, there is considerable interest in atmospheric suspended sulphates particles in view of their role in the radiation balance of the atmosphere and cloud microphysical processes, as well as their potential threat to human health.

The oxidation of sulphur dioxide in the atmosphere can occur both in the gas and aqueous phases. It is believed that clouds convert between 50 and 80% of SO_2 to H_2SO_4 in the troposphere [1] and that this process contributes substantially to the formation of acid rain. Atmospheric waters (wetted atmospheric aerosols and cloud, rain or fog droplets) represent a reactive medium where numerous chemical reactions may take place. One of important reactions is the oxidation of dissolved SO_2 with the available oxidants as H_2O_2, O_3 and O_2. Aqueous phase SO_2 oxidation by molecular oxygen catalysed with metal ions is considered as an important process for sulphuric acid/sulphate formation in the atmosphere.

Certain transition metal ions that are commonly found in the atmosphere catalyse the oxidation of dissolved SO_2 by dissolved oxygen. Therefore, a detailed knowledge of transition metal-catalysed SO_2 oxidation is essential in assessing the importance of aqueous phase SO_2 oxidation. Transition metal elements are abundant in the atmosphere with sources ranging from natural rock detritus to heavy metal industries. Even in the cleanest environments (oceans and polar regions) aerosols undergo heavy metal inclusion.

It is generally accepted, that iron(Il/llI) and manganese(II/III) are the most efficient catalysts [2 - 5]. The role of other redox active transition metal ions (copper [2, 6], cobalt [7, 8], chromium, and vanadium [9, 10] in the overall oxidation of sulfur(IV) in the tropospheric aqueous phase has not been fully elucidated so far.

Chromium is more abundant in the earth's crust than cobalt and copper. It is released into the environment in larger amounts as a result of human activities, which account for 60 - 70% of the total emissions of atmospheric chromium [11]. Any factory involved in the production or use of chemical compounds and alloys that contain chromium is a potential emitter of this metal to the environment. The burning of fuels, especially by power plants, is an industrial activity that represents a significant source of chromium.

Chromium concentrations in air vary with location. Typical concentrations of chromium at remote areas are less than1.0 ng/m^3 and average about 0.3 ng/m^3 [12]. The arithmetic mean concentrations of total chromium in the ambient air in United States, urban, suburban, and rural areas range from 5 to 525 ng/m^3, with the vast majority of samples < 100 ng/m^3 [13, 14]. In the immediate vicinity of industrial plants, chromium concentrations may be much higher, above 500 μg/m^3 [15].

In atmospheric precipitation samples collected in Hungary at sites which were not influenced directly by anthropogenic pollution sources, the concentrations of Cr(III) were found to be between 0.1 and 0.4 μg/dm^3 [9]. In the United States chromium concentrations are 0.2-1 μg/dm^3 in rainwater[13]. In atmospheric precipitation samples collected in Kano (Nigeria) the concentrations of chromium were correlated with the industrial activities of the metropolis, and maximum concentrations of chromium were above 1.1μg/dm^3 [16]. In fog- and cloud water chromium concentrations may be about 10 times higher than those in rainwater, and in wet aerosols they may be about 100 times higher [17, 18]. In the aqueous phase of plant plumes, chromium concentrations may be even higher.

Atmospheric chemistry is extremely complex and atmospheric modelling is important for understanding phenomena such as acid rain and secondary atmospheric aerosols. Modeller's predictions are as good as their inputs, and they require accurate kinetic parameters for a number of reactions. Those reactions might occur in the gas or aqueous phases. The oxidation reactions of SO_2 dissolved in the aqueous phase are still not fully understood or need to be described in greater detail.

Only a few studies of the oxidation of sulfur(IV) in the presence of chromium have appeared [9, 10], and there are no data concerning the influence of Cr(III) ions on the Mn(II)-catalysed S(IV) oxidation. The experimental conditions in the studies of Brandt and Elding [9] and Martins [10] were different from those used in the present work.

The aim of the present study was to determine the kinetics of S(IV) oxidation in aqueous solutions in the presence of Cr(III) and Mn(II) ions under conditions representative for atmospheric waters on highly polluted areas, and afterwards to assess the influence of Cr(III) ions on the S(IV) oxidation catalysed by Mn(II) ions.

Material 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 Cr(III) were prepared from $KCr(SO_4)_2$. 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 carried out 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 ^{o}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 itself.

To start the reaction, the air flow was turned on and just after that the Cr(III) solution was injected into the reactor. At selected time intervals the concentration of S(IV) was measured by a 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 6.0. The pH measurements were performed by an Orion pH meter

(Model 710A) combined with a glass electrode. The concentration of Cr(III) was determined by AVANTA PM atomic absorption spectrometer of the GBC.

The experiments were performed under the following conditions: [S(IV)] ≈ $1\cdot10^{-3}$ mol·dm^{-3}, $1\cdot10^{-6} \le$ [Cr(III)] $\le 5\cdot10^{-5}$ mol·dm^{-3}, $1\cdot10^{-6} \le$ [Mn(II)] $\le 1\cdot10^{-5}$ mol·dm^{-3}, initial pH 3.5 and 6.0, T = 25^{o}C.

Results and Discussion

Results of the kinetic measurements are shown in Figures 1 - 4 as the time dependence of $[\mathrm{S(IV)}]_t/[\mathrm{S(IV)}]_0$ ratios, where $[\mathrm{S(IV)}]_t$ is the concentration of S(IV) at time *t*, and $[\mathrm{S(IV)}]_0$ is the initial concentration of S(IV). Based on the measurement results, kinetic law parameters for the processes studied were determined. The rate of S(IV) oxidation has been described by the equation:

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

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 rates calculated for [S(IV)] = $1\cdot10^{-3}$ mol·dm^{-3} and various Mn(II) and Cr(III) concentrations as well as for different initial pH values are given in Table 2.

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

[Mn], mol·dm^{-3}	n			k_{obs}, (mol·dm^{-3})$^{(1-n)}$·s^{-1}		
	[Cr] = 0, mol·dm^{-3}	[Cr] = $1\cdot10^{-6}$, mol·dm^{-3}	[Cr] = $5\cdot10^{-6}$, mol·dm^{-3}	[Cr] = 0, mol·dm^{-3}	[Cr] = $1\cdot10^{-6}$, mol·dm^{-3}	[Cr] = $5\cdot10^{-6}$ mol·dm^{-3}
Initial pH = 3.5						
0	0	1.5	1.5	$1.33\cdot10^{-8}$	$1.29\cdot10^{-3}$	$1.09\cdot10^{-3}$
$1\cdot10^{-6}$	0	0	0	$3.91\cdot10^{-8}$	$7.43\cdot10^{-8}$	$5.09\cdot10^{-8}$
$5\cdot10^{-6}$	0	0	0	$9.44\cdot10^{-8}$	$1.33\cdot10^{-7}$	$1.14\cdot10^{-7}$
$1\cdot10^{-5}$	0	0	0	$3.20\cdot10^{-7}$	$2.73\cdot10^{-7}$	$2.52\cdot10^{-7}$
Initial pH = 6.0						
0	2	6	5.5	$1.49\cdot10^{-1}$	$4.98\cdot10^{11}$	$1.61\cdot10^{10}$
$1\cdot10^{-6}$	3	3	-	$7.00\cdot10^{2}$	$5.91\cdot10^{2}$	-
$5\cdot10^{-6}$	2	0.9	-	2.40	$1.91\cdot10^{-4}$	-

Table 2. Rates and their ratios for the S(IV) oxidation catalysed by Mn(II) and Cr(III) ions at [S(IV)] = $1\cdot10^{-3}$ mol·dm^{-3}

[Mn], mol·dm^{-3}	**r, mol·dm^{-3} ·s^{-1}**			**$r_{(Mn + Cr)}/r_{Mn}$**		**$r_{(Mn + Cr)}/(r_{Mn} + r_{Cr})$**	
	[Cr] = 0, mol·dm^{-3}	**[Cr] = $1\cdot10^{-6}$, mol·dm^{-3}**	**[Cr] = $5\cdot10^{-6}$, mol·dm^{-3}**	**[Cr] = $1\cdot10^{-6}$, mol·dm^{-3}**	**[Cr] = $5\cdot10^{-6}$, mol·dm^{-3}**	**[Cr] = $1\cdot10^{-6}$, mol·dm^{-3}**	**[Cr] = $5\cdot10^{-6}$, mol·dm^{-3}**
Initial pH = 3.5							
0	$1.33\cdot10^{-8}$	$4.08\cdot10^{-8}$	$3.45\cdot10^{-8}$	-	-	-	-
$1\cdot10^{-6}$	$3.91\cdot10^{-8}$	$7.43\cdot10^{-8}$	$5.09\cdot10^{-8}$	1.90	1.30	$9.29\cdot10^{-1}$	$6.92\cdot10^{-1}$
$5\cdot10^{-6}$	$9.44\cdot10^{-8}$	$1.33\cdot10^{-7}$	$1.14\cdot10^{-7}$	1.41	1.21	$9.86\cdot10^{-1}$	$8.86\cdot10^{-1}$
$1\cdot10^{-5}$	$3.20\cdot10^{-7}$	$2.73\cdot10^{-7}$	$2.52\cdot10^{-7}$	0.85	0.79	$7.56\cdot10^{-1}$	$7.10\cdot10^{-1}$
Initial pH = 6.0							
0	$1.49\cdot10^{-7}$	$4{,}98\cdot10^{-7}$	-	-	-	-	-
$1\cdot10^{-6}$	$7.00\cdot10^{-7}$	$5.91\cdot10^{-7}$	-	0.97	-	$5.33\cdot10^{-1}$	-
$5\cdot10^{-6}$	$2.40\cdot10^{-6}$	$8.82\cdot10^{-8}$	-	$3{,}68\cdot10^{-2}$	-	$3.04\cdot10^{-2}$	-

The S(IV) oxidation in the presence of Cr(III) ions only

At an initial pH of 3.5, the S(IV) oxidation in the presence of Cr(III) ions is rather slow, only 20 - 23% S(IV) is oxidised after 100 minutes (Figures 1 – 3, curves for Cr(III) ions only). At an initial pH of 6.0, the reaction proceeds a little faster, and about 47 – 56% S(IV) is oxidised after the same time (Figure 4).

The rates of the S(IV) oxidation in the presence of Cr(III) ions (r_{Cr}) are in the range of $3.45\cdot10^{-8}$ – $4.98\cdot10^{-7}$ mol·dm^{-3}·s^{-1}, depending on Cr(III) concentrations and initial pH values (Table 2, *r* for [Mn(II)] = 0). At an initial pH of 3.5, the oxidation rate is small and ranges between $3.45\cdot10^{-8}$ and $4.08\cdot10^{-8}$ mol·dm^{-3}·s^{-1}, while at an initial pH of 6.0, the reaction rate increases to $4.98\cdot10^{-7}$ mol·dm^{-3}·s^{-1} at Cr(III) concentration of $1\cdot10^{-6}$ mol·dm^{-3}. The rate of S(IV) oxidation in the presence of Cr(III) ions is somewhat greater than that of the uncatalysed oxidation (Table 2, *r* for [Mn] = 0, [Cr] = 0).

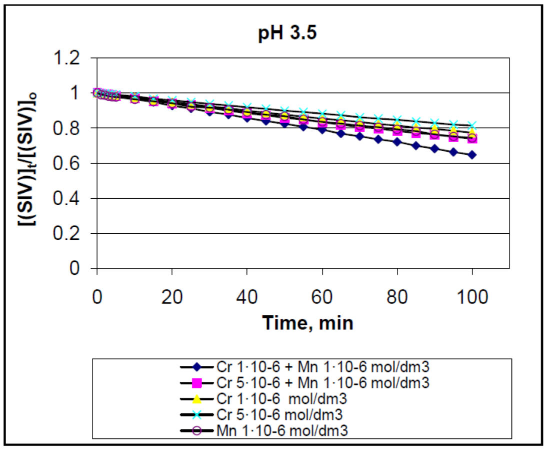

Figure 1: Effect of Cr(III) ions on the Mn(II)-catalysed S(IV) oxidation at initial pH 3.5, [Mn(II)] = 1·10^{-6} mol·dm^{-3}

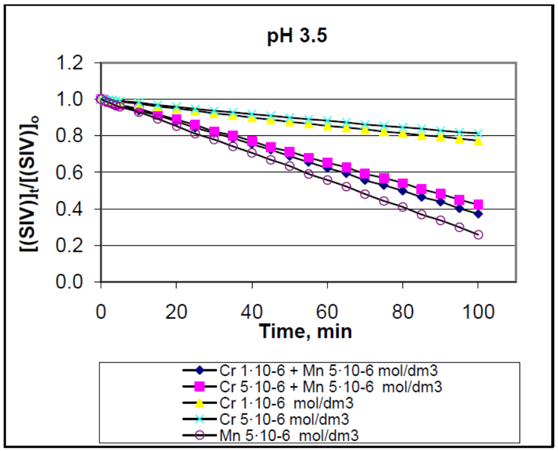

Figure 2: Effect of Cr(III) ions on the Mn(II)-catalysed S(IV) oxidation at initial pH 3.5, [Mn(II)] = 5·10^{-6} mol·dm^{-3}

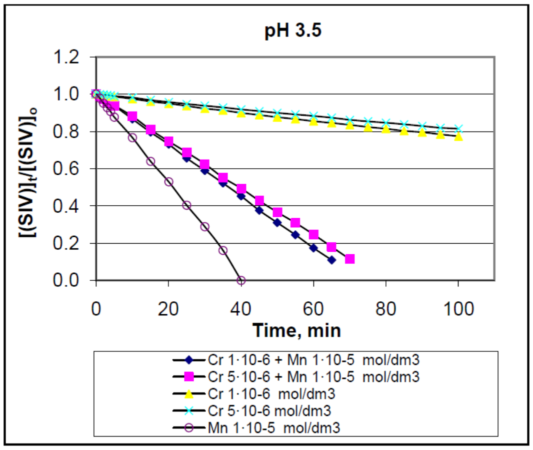

Figure 3: Effect of Cr(III) ions on the Mn(II)-catalysed S(IV) oxidation at initial pH 3.5, [Mn(II)] = 1·10^{-5} mol·dm^{-3}

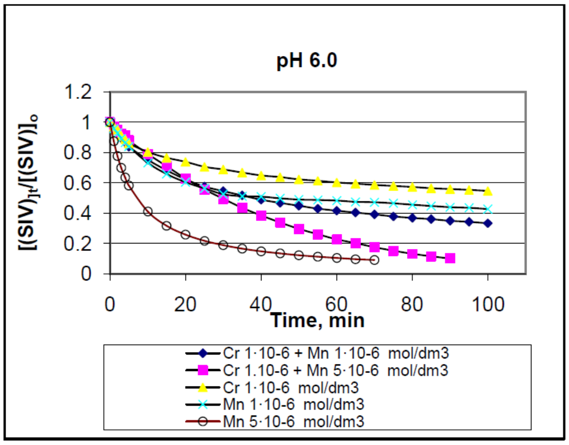

Figure 4: Effect of Cr(III) ions on the Mn(II)-catalysed S(IV) oxidation at initial pH 6.0, [Mn(II)] = 1·10^{-6} and 5·10^{-6} mol·dm^{-3}

To assess catalytic activity of Cr(III), the ratios of the Cr(III)-catalysed to the uncatalysed oxidation rates (r_{Cr}/r_n) were calculated (Table 2). The ratios vary from 2.60 to 3.35, depending on Cr(III) concentrations and initial pH values. This indicates that Cr(III) ions have little catalytic effect on the S(IV) oxidation. Under the experimental conditions, the catalytic activity of Cr(III) ions is not affected very much by changes in initial pH values and Cr(III) concentrations. The catalytic activity of Cr(III) ions is smaller than that of Mn(II) ions under the same conditions. For example, at initial pH of 3.5 and Cr(III) concentration of 5·10^{-6} mol·dm^{-3}, the r_{Cr}/r_n ratio is 2.6, whereas the r_{Mn}/r_n ratio is 7.1.

The S(IV) oxidation in the presence of both Cr(III) and Mn(II) ions

The results listed in Table 2 show that the rate of the S(IV) oxidation in the presence of both Mn(II) and Cr(III) ions ($r_{(Mn+Cr)}$) is somewhat greater or smaller than that in the presence of Mn(II) ions only (r_{Mn}), depending on initial pH values and concentrations of Mn(II) and Cr(III) ions.

To estimate the effect of Cr(III) ions on the S(IV) oxidation catalysed by Mn(II) ions, ratios $r_{(Mn+Cr)}/r_{Mn}$ were calculated (Table 2). At an initial pH of 3.5, the S(IV) oxidation in the presence of both Mn(II) and Cr(III) ions is about 1.2 – 1.9 times faster than that in the presence of Mn(II) ions only. At an initial pH of 6.0, the Mn(II)-catalysed S(IV) oxidation is practically unaffected by Cr(III) ions at Mn(II) and Cr(III) concentrations of 1·10^{-6} mol·dm^{-3}, while at Mn(II) concentration of 5·10^{-6} mol·dm^{-3}, the presence of Cr(III) ions causes strong decrease (about 27-fold) in the S(IV) oxidation rate. Under such conditions, the

S(IV) oxidation rate is even smaller than that of the uncatalysed S(IV) oxidation.

However, in all the cases, even when $r_{(Mn+Cr)}/r_{Mn} > 1$, the rate of the S(IV) oxidation in the presence of both Mn(II) and Cr(III) ions is smaller than expected from the sum of the two individual rates ($r_{(Mn+Cr)}/(r_{Mn}+r_{Cr}) < 1$), which shows that there is antagonism between Mn(II) and Cr(III) ions. The magnitude of the antagonistic effect depends on the initial pH and concentrations of both Mn(II) and Cr(III) ions. This effect increases with increase in both the initial pH and concentrations of Mn(II) and Cr(III) ions. The antagonistic effect is insignificant at an initial pH of 3.5, Mn(II) concentrations of $1 \cdot 10^{-6}$ - $5 \cdot 10^{-6}$ mol·dm^{-3}, and Cr(III) concentration of $1 \cdot 10^{-6}$ mol·dm^{-3}. For an initial pH of 3.5, the antagonistic effect becomes visible only at higher concentrations of Mn(II) and Cr(III) ions ($1 \cdot 10^{-5}$ and $5 \cdot 10^{-6}$ mol·dm^{-3}, respectively). At an initial pH of 6.0, the antagonistic effect is greater than that at an initial pH of 3.5, especially at higher concentration of Mn(II) ($5 \cdot 10^{-6}$ mol·dm^{-3}).

At lower Mn(II) concentration ($1 \cdot 10^{-6}$ mol·dm^{-3}), the antagonistic effect is insignificant for Cr(III) concentration of $1 \cdot 10^{-6}$ mol·dm^{-3}, and becomes visible for Cr(III) concentration of $5 \cdot 10^{-6}$ mol·dm^{-3} (the rate of the S(IV) oxidation in the presence of both Mn(II) and Cr(III) ions is about 2 times smaller than the sum of the two individual rates). At higher Mn(II) concentration ($5 \cdot 10^{-6}$ mol·dm^{-3}), the antagonistic effect is considerably higher, even at low Cr(III) concentration of $1 \cdot 10^{-6}$ mol·dm^{-3}. Under such conditions, the rate of the S(IV) oxidation in the presence of both Mn(II) and Cr(III) ions is 33 times smaller than the sum of the two individual rates.

Conclusion

Cr(III) ions show some catalytic activity in the S(IV) oxidation process. The rate of the S(IV) oxidation is 2.2 to 3.4 times greater than that of the uncatalysed oxidation over the studied range of Cr(III) concentrations ($1 \cdot 10^{-6}$ - $1 \cdot 10^{-5}$ mol·dm^{-3}) and initial pH values (3.5 - 6.0). The catalytic activity of Cr(III) ions is several times smaller than that of Mn(II) ions.

The rate of the S(IV) oxidation in the presence of both Mn(II) and Cr(III) ions is somewhat greater or smaller than that in the presence of Mn(II) ions only, depending on initial pH values and concentrations of Mn(II) and Cr(III) ions. At an initial pH of 3.5, the S(IV) oxidation is about 1.2 – 1.9 times faster than in the presence of Mn(II) ions only. At an initial pH of 6.0, the Mn(II)-catalysed S(IV) oxidation is practically unaffected by Cr(III) ions at Mn(II) and Cr(III) concentrations of $1 \cdot 10^{-6}$ mol·dm^{-3}, while at Mn(II) concentration of $5 \cdot 10^{-6}$ mol·dm^{-3}, the presence of Cr(III) ions causes very strong decrease in the S(IV) oxidation rate.

The rate of the S(IV) oxidation in the simultaneous presence of Mn(II) and Cr(III) ions is lower than expected from the sum of the two independent rates, i.e. there is catalytic antagonism between Mn(II) and Cr(III) ions. The antagonistic effect is small at an initial pH of 3.5. At an initial pH of 6.0, the antagonistic effect is also small at low Mn(II) and Cr(III) concentrations ($1 \cdot 10^{-6}$ mol·dm^{-3}), while at higher Mn(II) concentration ($5 \cdot 10^{-6}$ mol·dm^{-3}), it is considerably stronger.

The results obtained indicate that though Cr(III) alone have some catalytic activity in the S(IV) oxidation process, it might reduce the total oxidation of S(IV) in the atmosphere where various metals are present simultaneously, among those Mn(II) and Cr(III). It might especially occur at higher atmospheric water pH and concentrations of Mn(II) and Cr(III).

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