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Influence of NO_2 and metal ions on oxidation of aqueous-phase S(IV) in atmospheric concentrations

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ABSTRACT

An investigation was made of the influence of atmospheric concentrations (15 or 130 ppbv) of NO_2 on the aqueous-phase oxidation rate of S(IV) in the presence and absence of Fe(III), Mn(II) and Cr(VI) metal ions under controlled experimental conditions (pH, T, concentration of reactants, etc.). The reaction rate in the presence of the NO_2 flow was slower than the reaction rate using only clean air with an initial S(IV) concentration of 10^{-4} mol/L. NO_2 appears to react with S(IV), producing a kind of inhibitor that slows down the reaction. Conversely, tenfold lower concentrations of S(IV) ($[S(IV)]_\circ = 10^{-5}$ mol/L) caused a faster reaction in the presence of NO_2 than the reaction using purified air. Under these conditions, therefore, the equilibrium shifts to sulfate formation. With the addition of Fe(III), Mn(II) or Cr(VI) in the presence of a NO_2 flow, the reaction occurred faster under all the conditions in which S(IV) oxidation was investigated.

Key words: aqueous S(IV) oxidation, metal ions, NO_2, acid rain formation.

INTRODUCTION

The process of sulfur dioxide oxidation plays an important role in atmospheric chemistry (e.g., formation of acid rain and degradation of visibility) (Eathoug et al. 1994, Cox et al. 1986). $SO_{2(g)}$ is known to react very slowly to produce $SO_{3(g)}$ at 400°C. Thus, $SO_{2(g)}$ oxidation in the atmosphere, either homogeneously in the gas phase or heterogeneously in an aqueous-phase, must be associated with other reaction processes such as photochemical oxidation or catalytic oxidation. These processes depend on a variety of factors, such as the intensity of incident solar radiation, relative air humidity, and particularly the presence of various oxidants (e.g., O_3, H_2O_2, NO_x, OH radicals) and transition metal ions that are known to act as catalysts (Martin 1984, Zuo and Zhan 2005).

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Reports of the oxidation of S(IV) in aqueous phase by oxygen catalyzed by transition metals usually involve metal ions such as Fe(III), Mn(II), Cu(II),Co(II), Ni(II), Cr(VI). It has been shown that catalytic activity depends on the pH, and that iron and manganese are the most effective catalysts. The presence of other oxidants, such as H_2O_2, O_3 or NO_x, in the oxidation of aqueous S(IV) has been studied in the laboratory, in the presence and absence of metal ions; however, much of the work involved oxidant concentrations several times higher than those typically found in urban atmospheres (Brandt and van Eldik 1995, Tursic et al. 2001, Clifton et al. 1988). Estimated S(IV) aqueous oxidation rates indicate that H_2O_2 is expected to be the most important oxidant for S(IV) in clouds and fogs at $pH < 4.5$. At higher pH values, O_3 and the catalytic effect of iron can compete (Martin 1984).

Nitrogen oxides (NO, NO_2, NO_3, HNO_2 e HNO_3) have all been suggested as possible oxidizing agents for dissolved S(IV) (Finlayson-Pitts and Pitts 2000 and references therein). In aqueous solution, HNO_2 reacts with S(IV) at a reasonable rate; however, the levels of gaseous HNO_2 observed in ambient air yield aqueous concentrations that are too low to contribute substantially to aqueous phase S(IV) oxidation. Whether dissolved NO_2 contributes significantly to the oxidation of S(IV) in solution is uncertain (Finlayson-Pitts and Pitts 2000 and references therein). Nitrogen dioxide is relatively insoluble; however, based on data reported in the literature, Schwartz and White (1983) inferred that the rate constants for the reaction of NO_2 with HSO_3^- and SO_3^{2-} may be sufficiently high to produce significant NO_2-S(IV) reactions.

In this study, we investigated S(IV)-NO_2 oxidation in aqueous phase in the presence and absence of Fe(III), Mn(II) and Cr(VI), in a concentration of S(IV), NO_2 and metal ions such as that found in an urban atmosphere (Grgcic et al. 1991, Alonso and Godinho 1992, Eatough et al. 1994, Finlayson-Pitts and Pitts 2000). Experiments were conducted at two distinct initial pH values, 3.7 and 5.2, which are typical atmospheric conditions. The concentration of SO_4^{2-} was monitored during the course of the reaction. Our interest in these reactions lies in their possible importance in atmospheric aqueous S(IV) oxidation processes.

MATERIALS AND METHODS

REAGENTS

All the chemicals used in this study were of analytic reagent grade and all the solutions were prepared using distilled water further purified in an E-pure system (Barnstead). Fresh solutions of $K_2Cr_2O_7$, $MnCl_2$ and $FeCl_3$ were used.

The analytical curve for SO_4^{2-} (concentration range: 1-5 mg/L or 0.1-0.5 mg/L) was prepared using reference solutions of K_2SO_4 1 mg/mL. For the kinetic studies, we used a fresh solution of SO_3^{2-} 1.2 mg /mL prepared from $Na_2S_2O_5$. The pH was adjusted using NaOH (0.1 mol/L) and HNO_3 (0.1 mol/L) solutions.

APPARATUS

The kinetic studies were conducted in a 500-mL round-bottomed reactor with three necks (24/40 joints) thermostatically controlled by means of a water bath. A Digimed Model DMPH-2 pH meter and an Analyzer 2A13/AM microglass electrode were used for determining the pH.

The concentration of SO_4^{2-} was determined using an ion chromatograph (IC) Dionex (Model 4000 i) equipped with a 500 μL Rheodyne injector and a conductivity detector at 30 μS. The analytical column was a Dionex AS9-SC followed by a Dionex AMMS-1 fibrous micromembrane suppressor. An eluant of 1.8 mmol/L $NaHCO_3$ + 1.7 mmol/L Na_2CO_3 was used at a flow rate of 2.0 mL/min and a pressure of 1300 psi.

The purified airflow was generated by a Zero Air Supplier (Thermo Environmental, model 111, equipped with a column of Purafil, a column of iodated charcoal and a reactor with catalytical surface). The NO_2 flow was produced using a permeation tube in a VICI Metronics Dynacalibrator, model 450. A mass flow meter (Haake Medingen GMBH) was used to control the flow rate.

PROCEDURES

Figure 1 illustrates the reactor used in these experiments. The three inlets of the reaction flask were used: (2) Rushton type turbine impeller, (3) introduction of reagents, and (4) introduction of gas. Aliquots of 1mL of metal ion solution (Fe(III), Mn(II) or Cr(VI)) were placed in the reactor and the pH (3.7 or 5.2) was immediately adjusted by adding variable amounts of NaOH or HNO_3 0.1 mol/L solutions. Then, 1.0 mL of fresh aqueous SO_3^{2-} solution was injected into the reactor at time (t = 0). The total volume of reaction solution was adjusted to 150 mL and the initial concentration of SO_3^{2-} was set at 8.0 mg $L^{-1}(10^{-4}$mol/L) or 0.8 mg $L^{-1}(10^{-5}$ mol/ L). The gas phase (purified air or NO_2) was then continuously bubbled through the aqueous solution at a flow rate of 1.0 mL/min. Both gas and liquid phases were well mixed in the reactor. Aliquots of 1 mL were removed at regular intervals, and 1 mL of formaldehyde solution (10^{-2} mol/L) was added immediately in order to quench S(IV) oxidation (de Andrade and Tanner 1992, de Andrade et al. 1993, 1995, Oliveira and de Andrade 1994). Thus, the oxidation reaction was stopped by the formation of hydroxymethanesulphonate, according to the following reaction (Eq. 1):

$$SO_3^{2-} + HCHO \rightarrow {}^{-}O_3SHCHO^{-} \tag{1}$$

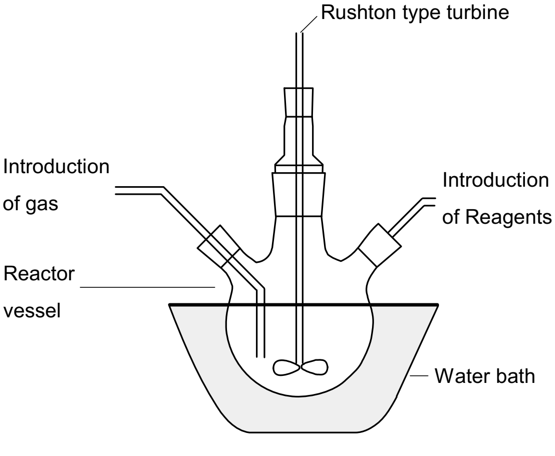


Fig. 1 – Apparatus for kinetics studies.

Once the stabilized solution was injected into the ion chromatography system, the sulfate signals (decomposition product of hydroxymethanesulphonate in mobile phase, basic media) were measured and the S(VI) concentrations were determined based on the corresponding calibration curve. For purposes of comparison, the S(IV) oxidation reaction was monitored under different conditions, which consisted of passing a purified air or NO_2 flow (15 or 130 ppbv) through the S(IV) solution (10^{-4} or 10^{-5} mol/L) in the absence and presence of transition metal ions. All the measurements were taken at 22°C. Special care was taken to ensure the purity of the water, because traces of transition metals remaining in the water as a result of deficiencies in the purification process can accelerate the reaction.

RESULTS AND DISCUSSION

REACTIONS IN THE PRESENCE OF NO_2 (15 OR 130 ppbv)

The S(IV) oxidation reaction in aqueous medium was first monitored in an initial S(IV) concentration of 8 mg/L (10^{-4} mol/L), in the absence of metal ions, and a NO_2 flow in a concentration of 15 or 130 ppb. The experiments were carried out in pH 3.7 and 5.2, with the temperature kept at 22°C. For comparison, the reaction was also monitored in the presence of purified air. Figures 2a and 2b illustrate the increase in the concentration of S(VI) along the reaction time under different conditions. The results indicated that the addition of NO_2 to the system hindered the oxidation of S(IV) at both pH 3.7 and pH 5.2, and that this effect was more marked at the higher NO_2 concentration. Note that the reactions show similar profiles for the two values of pH studied here.

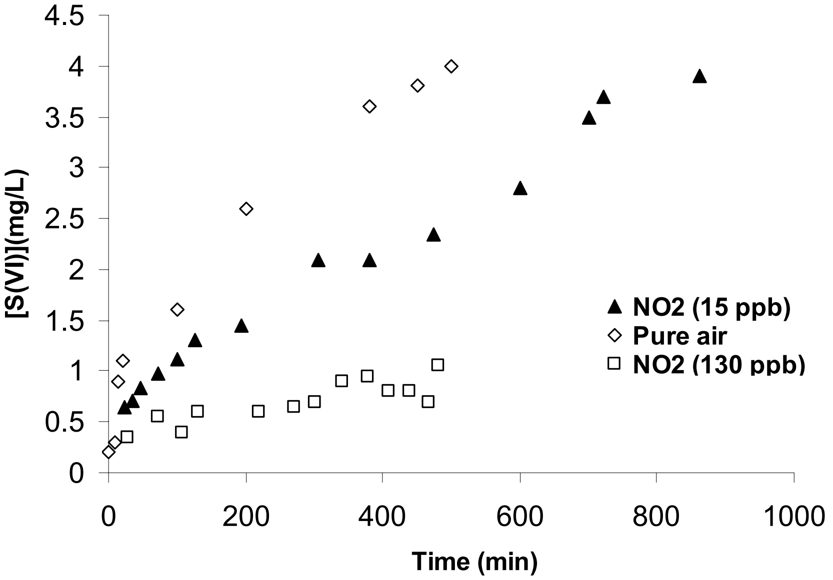


Fig. 2a – Time dependence of [S(VI)] for S(IV) oxidation, $[S(IV)]_o$ = 8 mg/L, pH = 5.2, T = 22°C.

Since it was outside not in the interest of this study to work with even higher NO_2 concentrations (improbable in the atmosphere), the reaction was also investigated at a tenfold lower initial concentration of S(IV), 10^{-5} mol/L (0,8 mg/L), with an NO_2 concentration of 130 ppb. Under these conditions, the exact opposite was found to occur, i.e., the S(IV) oxidation rate was higher in the presence of the airflow with NO_2 than in the presence of purified air (Fig. 3).

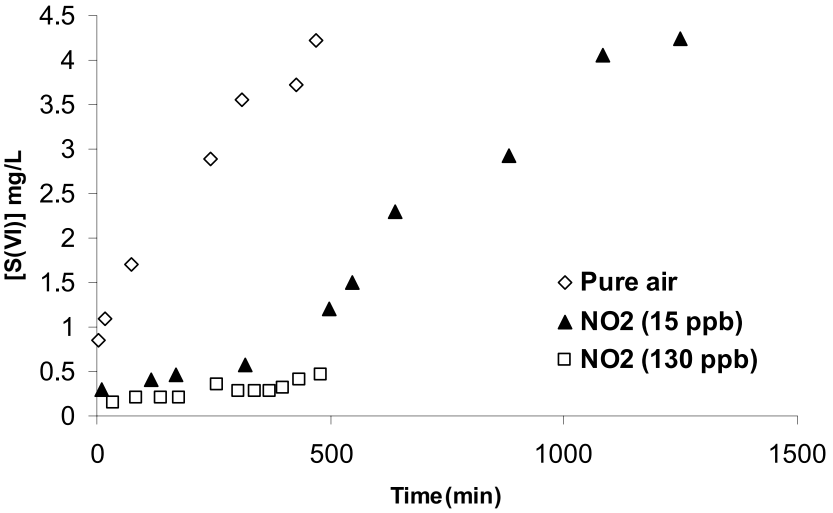


Fig. 2b – Time dependence of [S(VI)] for S(IV) oxidation, $[S(IV)]_o = 8$ mg/L, pH = 3.7, T = 22°C.

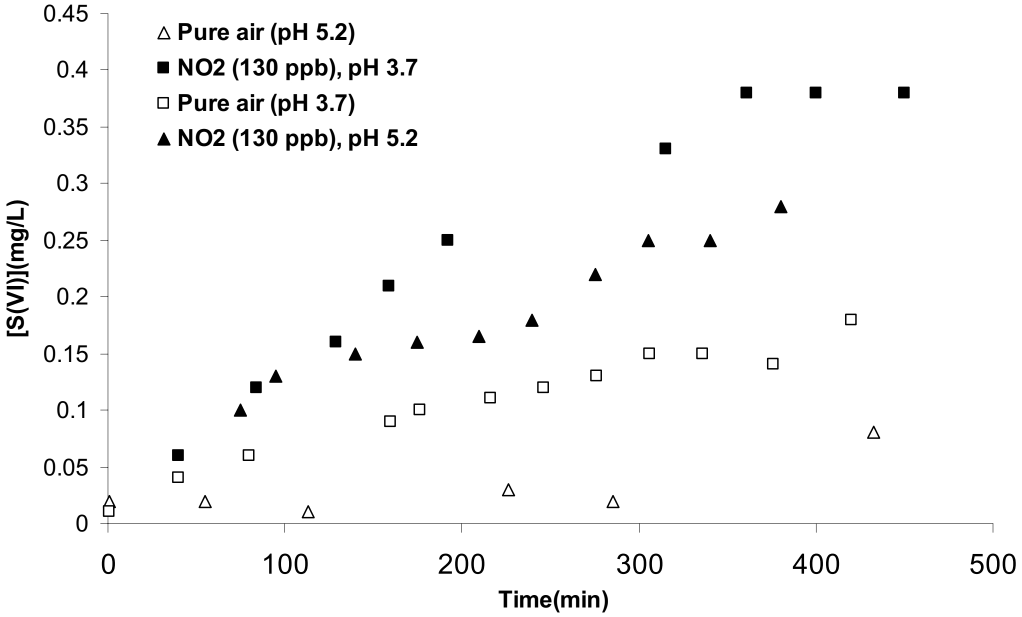


Fig. 3 – Time dependence of [S(VI)] for S(IV) oxidation, $[S(IV)]_o = 0.8$ mg/L, T = 22°C.

The mechanism whereby the reaction between NO_2 and SO_2 in aqueous solution occurs is complex and has been studied for many decades. The absorption of NO_2 in water leads to the formation of NO_2^- and NO_3^- ions. In acid solution, HNO_2/NO_2^- react with HSO_3^-/SO_2^{2-}, producing a mixture of N-S-oxides, intermediary species that can subsequently decompose, resulting in other end products (Oblath et al. 1982, Geißler and van Eldik 1994, Coichev and van Eldik 1994) (eqs. 2 to 9).

$$NO_2^- + H^+ = HONO \tag{2}$$

$$HONO + HSO_3^- \rightarrow NOSO_3^- + H_2O \tag{3}$$

$$ONSO_3^- + HSO_3^- \rightarrow HON(SO_3)_2^{2-} \tag{4}$$

$$2HSO_3^- = S_2O_5^{2-} + H_2O \tag{5}$$

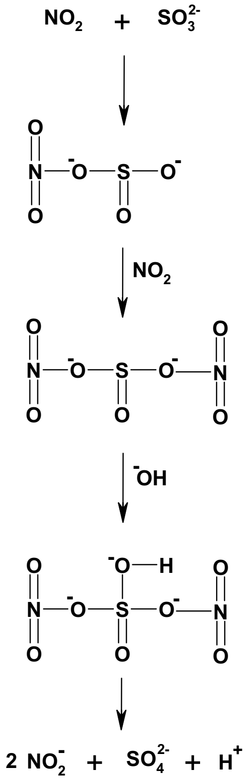
$$HONO + S_2O_5^{2-} \rightarrow HON(SO_3)_2^{2-} \tag{6}$$

$$HON(SO_3)_2^{2-} + HSO_3^- \rightarrow N(SO_3)_3^{3-} + H_2O \tag{7}$$

$$HON(SO_3)_2^{2-} + SO_3^{2-} \rightarrow HN(SO_3)_2^{2-} + SO_4^{2-} \tag{8}$$

$$HON(SO_3)_2^{2-} + H^+ + H_2O \rightarrow HONHSO_3^- + HSO_4^- \tag{9}$$

In another study, Clifton et al. (1988) determined the rate constant for the reaction between NO_2, SO_3^{2-} and HSO_3^- in aqueous solution (pH 5 to 13). Their observations suggested a mechanism involving the formation of an addition complex in an initial stage, which could, in a subsequent reaction, react with more NO_2 and form a second long life intermediary, which could then decompose, forming nitrite and sulfate (eq. 10). According to these authors, in the case of a very low NO_2 concentration, the reaction (10) would predominate. Thus, the addition of more NO_2 increases the probability of the formation of the second intermediary and of the equilibrium shifting toward the formation of sulfate.



(10)

The results of the present work suggest that the oxidation reaction of S(IV) in the aqueous phase in the presence of NO_2 may occur either more slowly than in the presence of purified air alone ($[S(IV)_\circ]$ = 8 mg/L, NO_2 15 ppbv or 130 ppbv). Alternatively, the oxidation reaction of S(IV) may occur at relatively lower values of S(IV) ($[S(IV)]_\circ$ = 0.8 mg/L and NO_2 130 ppbv). Taken together with data reported in the literature on studies of the oxidation of S(V) in the presence of NO_2, our results suggest that the mechanism may be an equilibrium involving the formation of long-lived intermediary species that hinder the progress of the reaction. However, at a relatively higher NO_2 concentration, the intermediary species could undergo decomposition, causing the equilibrium to be rapidly shifted towards sulfate formation, thus favoring the reaction.

REACTIONS IN THE PRESENCE OF NO_2 AND METAL IONS

We began by studying the S(IV) oxidation reaction in the presence of NO_2 (15 ppbv) and Fe(III), Mn(II) and Cr(VI) metal ions for an initial S(IV) concentration of 8 mg/L. The metal ion concentrations used here were 0.10 mg/L, 0.12 mg/L and 1.0 mg/L for Mn(II), Fe(III) and Cr(VI), respectively. Figures 4a and 4b show the concentrations of S(VI) along the reaction under distinct conditions, with a NO_2 concentration of 15 ppb. As can be seen, the Fe(III), Mn(II) and Cr(VI) ions display a catalytic activity in the oxidation reaction of S(IV) in aqueous phase, an effect that predominates over the inhibiting effect of NO_2. The reaction in the presence of Fe(III) at pH 5.2 was not studied, since the catalytic activity of this ion drops sharply under these conditions (Grgic et al. 1991). At a higher concentration of NO_2 (130 ppb) and initial concentration of S(IV) of 8 mg/L – the condition in which NO_2 showed an even stronger inhibiting effect on the oxidation of S(IV) (Figures 2a and 2b) – the reaction was also monitored in the presence of the ions that presented the highest catalytic activity, Fe(III) and Mn(II). Figure 5 depicts the increase in S(IV) along the reaction for pH 3.7. Once again, it is clear that the effect of the metal ions studied here predominates over that of NO_2 in this type of reaction.

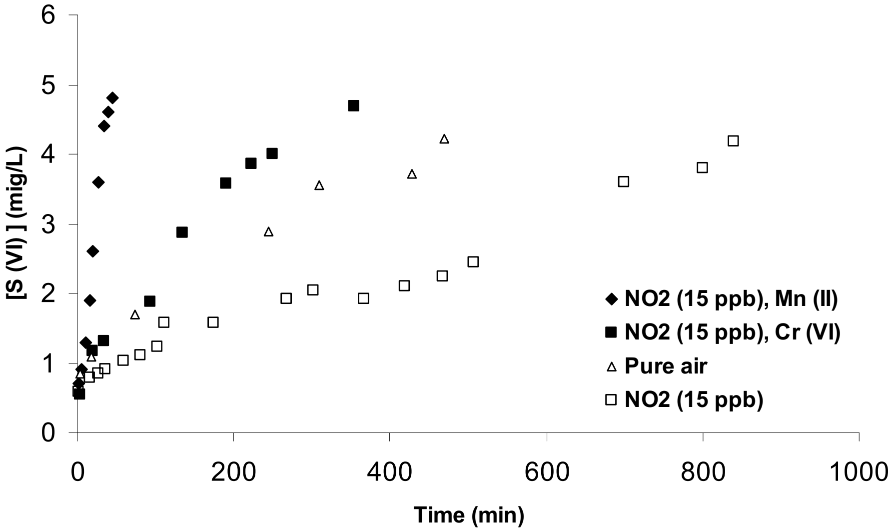


Fig. 4a – Time dependence of [S(VI)] for S(IV) oxidation, $[S(IV)]_\circ$ = 8 mg/L, pH = 5.2, T = 22°C.

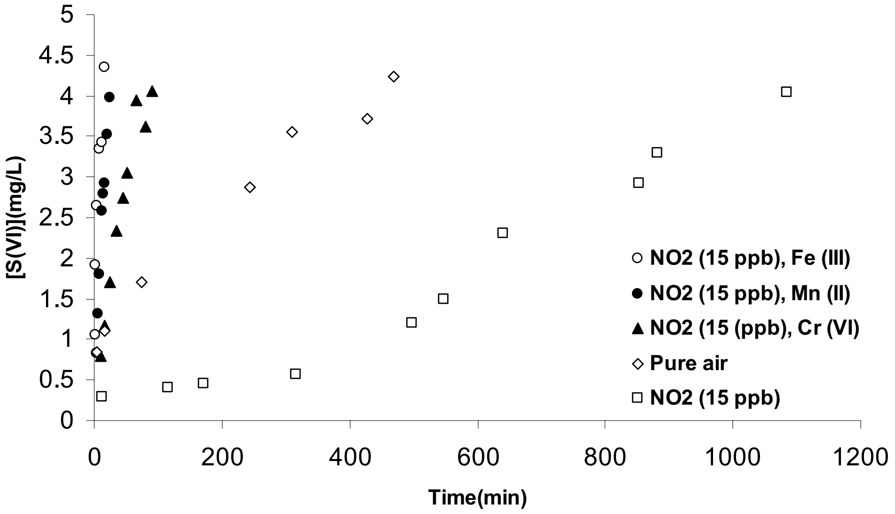


Fig. 4b – Time dependence of [S(VI)] for S(IV) oxidation, $[S(IV)]_o$ = 8 mg/L, pH = 3.7, T = 22°C.

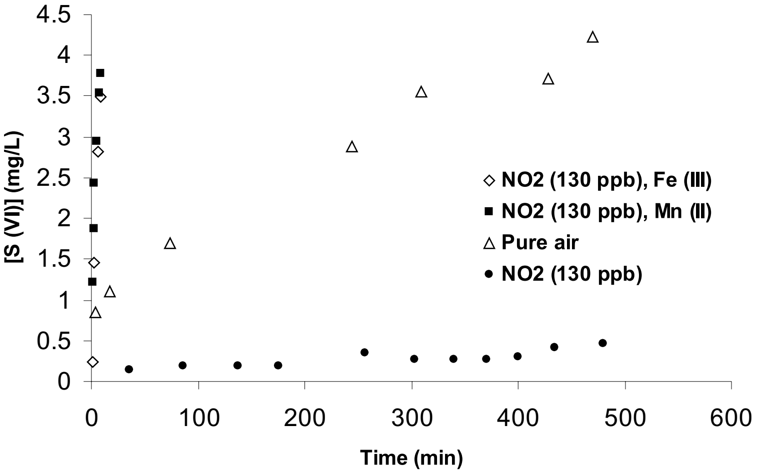


Fig. 5 – Time dependence of [S(VI)] for S(IV) oxidation, $[S(IV)]_o$ = 8 mg/L, T = 22°C, pH = 3.7.

At the higher concentration of 130 ppb of NO_2 and an initial concentration of S(IV) of 0.8 mg/L, i.e., the condition in which NO_2 was found to accelerate the oxidation of S(IV), the reaction was also monitored in the presence of Fe(III) and Mn(II) ions, but with a tenfold reduction in the concentration of metal ions (Fig. 6). The results indicated that, in the presence of NO_2 and metal ions, the S(IV) oxidation reaction rate increased even further than in the presence of only NO_2, demonstrating that in this condition, too, the catalytic activity of the ions predominates in this type of reaction.

The catalytic activity of transition metal ions in the S(IV) oxidation process has been studied by various researchers (Brandt and van Eldik 1995). Despite the lack of a consensus about which metals are more active catalyzers in this type of reaction, Fe(III) and Mn(II) ions appear to be the strongest candidates, followed by others such as Cu(II), Co(II) and Ni(II) (Martin 1984, Brandt and van Eldik 1995). Studies conducted

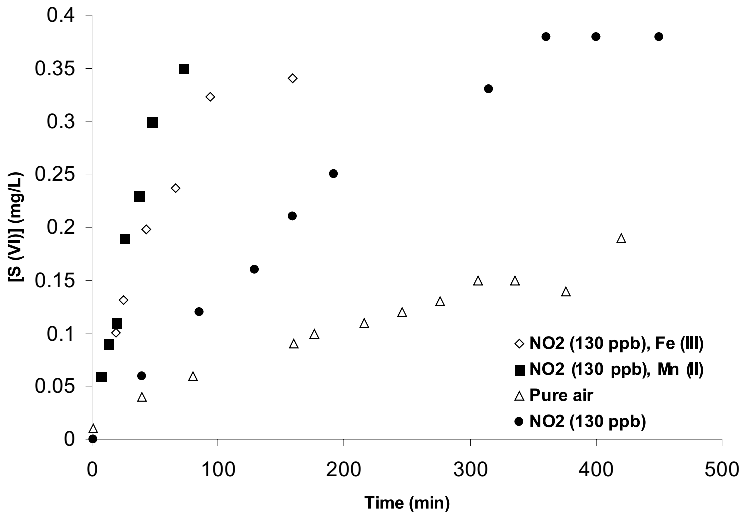


Fig. 6 – Time dependence of [S(VI)] for S(IV) oxidation, $[S(IV)]_o = 8$ mg/L, T = 22°C, pH = 3.7.

by Brandt and Elding (1998) and Martins et al. (1999) also revealed the catalytic activity of Cr(VI) ions in this type of reaction. The mechanism whereby homogeneous catalysis by transition metals occurs has been widely discussed in the literature, with the majority of reports explaining the process based on the free radical mechanism, a necessary condition being that the ion display multiple oxidation states. Metal ions in a higher state of oxidation can extract electrons from the S(IV) species, generating radicals which, in turn, can propagate the reaction. The reduced metal species should be able to return to the higher oxidation state, initiating the process anew. There must therefore be an energetically favorable stage in which the reduced metal ion returns to a higher state of oxidation. This has been an important and widely discussed aspect: how the reduced metal species is then re-oxidized, completing the catalytic cycle. The majority of authors suggest that the reduced metal ion is reoxidated by the very radicals formed in the process. In the case of Fe(II)/Fe(III), one of the systems with the highest catalytic activity, Brandt and coworkers (1994) propose the following scheme of reactions in a radical chain mechanism:

$$\mathrm{Fe(III)} + \mathrm{nHSO_3^-} = \mathrm{Fe^{III}(HSO_3^-)_n^{3\text{-}n}} \quad (\mathrm{n} = 1, 2, 3) \tag{11}$$

Reduction $$\mathrm{Fe^{III}(HSO_3^-)_n^{3\text{-}n}} \rightarrow \mathrm{Fe(II)} + (\mathrm{n}-1)\mathrm{HSO_3^-} + \mathrm{H^+} + \mathrm{SO_3^{\bullet-}} \tag{12}$$

$$\mathrm{Fe(III)} + \mathrm{SO_3^{\bullet-}} + \mathrm{H_2O} \rightarrow \mathrm{Fe(II)} + \mathrm{HSO_4^-} + \mathrm{H^+} \tag{13}$$

$$\mathrm{SO_3^{\bullet-}} + \mathrm{O_2} \rightarrow \mathrm{SO_5^{\bullet-}} \tag{14}$$

$$\mathrm{SO_5^{\bullet-}} + \mathrm{HSO_3^-} \rightarrow \mathrm{SO_3^{\bullet-}} + \mathrm{HSO_5^-} \tag{15}$$

$$\mathrm{Fe(II)} + \mathrm{SO_5^{\bullet-}} + \mathrm{H^{++}} \rightarrow \mathrm{Fe(III)} + \mathrm{HSO_5^-} \tag{16}$$

Oxidation $$\mathrm{Fe(II)} + \mathrm{HSO_5^-} \rightarrow \mathrm{Fe(III)} + \mathrm{SO_4^{\bullet-}} + \mathrm{OH^-} \tag{17}$$

$$\mathrm{Fe(II)} + \mathrm{SO_4^{\bullet-}} + \mathrm{H^+} \rightarrow \mathrm{Fe(III)} + \mathrm{HSO_4^-} \tag{18}$$

$$\mathrm{SO_4^{\bullet-}} + \mathrm{HSO_3^-} \rightarrow \mathrm{SO_3^{\bullet-}} + \mathrm{HSO_4^-} \tag{19}$$

The first reactions represent the reduction of the sulfite-Fe(III) complexes. After that, the $SO_3^{\bullet -}$ radical can both reduce the Fe(III) species and rapidly form the $SO_5^{\bullet -}$ radical in the presence of oxygen. The $SO_5^{\bullet -}$ radical is a strong oxidant (E $SO_5^{\bullet}/HSO_5^-$ = 1.1 V, pH 7), which, in a series of reactions, can again oxidize Fe(II) to Fe(III), completing the catalytic cycle.

If NO_2 is present together with Fe(III), the global mechanism for S(IV) oxidation becomes complicated by the possibility of several routes. In addition to the aforementioned mechanisms, there is the possibility of interaction between metal species and dissolved NO_2. In the case of the Fe(II)/Fe(III) system, the reduced metal ion can promote an interaction between HNO_2/NO_2^- and HSO_3^-, generating a new catalytic cycle (Coichev and van Eldik 1994). Additionally, Fe(III) may react with the mixture of N-S oxides, which could, in principle, inhibit the catalytic oxidation of S(IV) by Fe(III) (Lepentsiotis et al. 1996). In a study conducted by Trsic et al. (2000) on the influence of Fe(III) and NO_2 on the oxidation of aqueous-phase S(IV) using high concentrations of NO_2 (0.84 and 1.68 ppm), it was found that oxidation appears to occur by two independent routes: SO_2/NO_2/air and SO_2/NO_2/air/Fe(III), but the results indicated that the most important effect is the catalytic effect of Fe(III).

In the present study, under all the conditions in which the oxidation reaction of S(IV) in the presence of NO_2 and Fe(III), Mn(II) and Cr(VI) was monitored, it was also found that the catalytic activity of the metal ions played a predominant role in the system, even under the conditions in which NO_2 slowed down the S(IV) oxidation rate, thus demonstrating their preponderance over the possible inhibitory effect of NO_2 on the reaction.

CONCLUSIONS

The aqueous-phase S(IV) oxidation rate in the presence of NO_2 depends on the relative concentrations of both chemical species. The addition of a NO_2 flow in a concentration of 15 or 130 ppb slowed down the aqueous-phase S(IV) oxidation rate for an initial S(IV) concentration of 10^{-4} mol/L (8 mg/L) in the presence of purified air, in both pH 3.7 and 5.2. However, in a tenfold lower initial S(IV) concentration of 10^{-5} mol/L and a NO_2 flow of 130 ppb, the reaction rate was favored when compared to the reaction in the presence of purified air. The explanation for this appears to be the existence of an equilibrium involving the formation of intermediary long life species, which could hinder the progress of the reaction. However, depending on the relative concentrations of S(IV) and NO_2, these species could decompose, causing the equilibrium to shift toward the formation of sulfate.

The addition of Fe(III), Mn(II) and Cr(VI) metal ions in the presence of NO_2 increased the sulfate formation rate under all the conditions studied here, indicating that these ions play a determining role in the S(IV) oxidation process.

In polluted urban atmospheres where the presence of S(IV) species, metal ions, and NO_2 in concentrations similar to those studied here is common, the oxidation of aqueous-phase S(IV) may be favored or not, depending on the relative concentrations of S(IV) and NO_2. In the presence of metal ions, which are species increasingly present in the atmospheric aqueous phase, these ions seem to predominate in the process, and the more common ions such as Fe(III) and Mn(II) must strongly catalyze the reaction, rapidly shifting the equilibrium toward the formation of sulfate.

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RESUMO

A reação de oxidação de S(IV) em fase aquosa foi estudada em laboratório em presença de NO_2 dos íons metálicos Fe(III), Mn(II), e Cr(VI) sob condições experimentais controladas (pH, T, concentração dos reagentes, etc.). Na presença de corrente de ar com NO_2 (15 ou 130 ppbv) a reação de oxidação de S(IV) ocorreu mais lentamente do que na presença de ar purificado, para uma concentração inicial de S(IV) de 10^{-4} mol/L. Ao contrário, para concentração inicial de S(IV) dez vezes menor ($[S(IV)]_{\circ} = 10^{-5}$ mol/L) a reação ocorreu mais rapidamente na presença de NO_2. A explicação está relacionada com o equilíbrio envolvendo a formação de espécies intermediárias de longa vida, que impedem o prosseguimento da reação, porém a depender das concentrações relativas de S(IV) e NO_2, essas espécies se decompõem deslocando o equilíbrio no sentido de formação de sulfato. A adição dos íons Fe(III), Mn(II) ou Cr(VI) em presença de corrente de ar com NO_2 indicou atividade catalítica para esses íons, em todas as condições nas quais a oxidação de S(IV) foi investigada.

Palavras-chave: oxidação de S(IV), íons metálicos, NO_2, formação de chuva ácida.

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