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A mechanistic study of the sulfite-induced autoxidation of Mn(II) in aqueous azide medium

Nina Coichev* and **Rudi van Eldik****

Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten (F.R.G.)

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Abstract

The sulfite-induced autoxidation of Mn(II) was studied in aqueous azide medium as a function of the Mn(II), Mn(III), S(IV) and O_2 concentrations. The reaction exhibits autocatalytic behaviour and requires the presence of Mn(III) in order to be effective. The O_2, Mn(II) and S(IV) concentrations determine whether only oxidation of Mn(II) to Mn(III), or reduction of Mn(III) to Mn(II), or both processes in one or two redox cycles, is observed.

Introduction

Metal ions and complexes of Fe(III), Co(III) and Mn(III) are generally known to be potential catalysts in the oxidation of sulfur(IV) oxides by dissolved oxygen [1–4]. The metal species typically react with sulfite to produce the sulfite radical SO_3^- and the reduced metal species. The sulfite radical then initiates a chain reaction which results in the formation of the final oxidation products. A crucial aspect of the overall catalytic cycle is the way in which the reduced metal species is reoxidized to the initial state. In general the oxidation of the metal species by dissolved oxygen is too slow to account for the observed catalytic effects. In a number of earlier studies, indirect evidence and arguments were presented in favour of a sulfite-induced autoxidation reaction of the reduced metal species [5–8]. We were involved in a series of recent studies dealing with the sulfite catalyzed autoxidation of aquated Fe(II) [9, 10], and of Co(II) in aqueous azide medium [11, 12]. Preliminary experiments demonstrated that the autoxidation process is further accelerated by the presence of Mn(II) in both systems [11, 13]. We have therefore undertaken a detailed study of the autoxidation of Mn(II) in aqueous azide medium induced by sulfur(IV) oxides.

Experimental

All reagents were of analytical reagent grade (Merck) and deionized water was used to prepare all solutions. N_2 was used to deaerate solutions where required. Stock solutions of sulfite were prepared by dissolving $Na_2S_2O_5$ in deaerated water and kept in a refrigerator at 5 °C [14]. Other stock solutions were prepared using NaN_3, $HClO_4$ (to adjust the pH), $NaClO_4$ (to adjust the ionic strength) and $Mn(ClO_4)_2$. A constant current source, adjustable at the mA level, was used in a H shaped coulometric cell to generate Mn(III) as described in detail before [15]. Typical Mn(III) concentrations generated in this way were *c.* 1×10^{-4} M during a 40 s electrolysis of 0.05 to 0.20 M Mn(II) in 1.0 M NaN_3 and HN_3 at pH 6.8. Solutions prepared in this way were stable for at least 3 days when stored in the dark at 5 °C.

pH measurements were performed on a Metrohm 632 pH meter equipped with a combined glass electrode. Kinetic measurements were performed on a Durrum D110 stopped-flow instrument equipped with an on-line data acquisition system [16], or in the thermostated cell compartment of a Shimadzu UV 250 spectrophotometer. The temperature control was within ±0.1 °C on both instruments.

Results and discussion

An earlier study [15] on the formation and stability of Mn(III) in azide medium, produced via the electrochemical oxidation of Mn(II), indicated that 1:1,

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*On leave from the Instituto de Quimica, Universidade de São Paulo, Cx. Postal 20780CEP 01498, São Paulo, Brazil.

**Author to whom correspondence should be addressed.

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1:2 and 1:3 Mn(II)–N_3 complexes are formed at azide concentrations up to 1.6 M. Significantly more stable Mn(III) complexes and of higher stoichiometry are expected to be produced under such conditions, based on that reported for the corresponding cobalt system [17]. Notwithstanding this information, the exact species distribution for the Mn(II/III) azide system is presently unknown. The electrochemically generated Mn(III) enabled us to obtain spectral data on the Mn(III)–azide complexes [15]. An absorption maximum is reached at 427 nm ($\epsilon = 6 \times 10^3$ M^{-1} cm^{-1}) in 0.5–2.0 M azide at pH 6.3, under which condition the absorption of Mn(II) is very small. The oxidation of Mn(II) to Mn(III) could therefore be followed at 427 nm.

Oxidation of Mn(II) to Mn(III) by dissolved oxygen in azide medium is extremely slow and competes with the reduction of Mn(III) by azide during which Mn(II) and N_2 are produced. Addition of sulfite significantly enhances the process when a small initial concentration of Mn(III) is present in solution. In the absence of initial Mn(III), the sulfite induced autoxidation of Mn(II) is also slow, presumably due to the autocatalytic nature of the process as found in the cobalt system [11, 12]. In the presence of initial Mn(III) the absorbance–time traces, representing the oxidation of Mn(II) to Mn(III), exhibit some autocatalytic behaviour in the initial part of the curve. A typical example is given in Fig. 1(a). The stability of the produced Mn(III) species depends on the employed sulfite and Mn(II) concentrations. At lower Mn(II) concentration (Fig. 1(b)) the formation of Mn(III) is followed by the reduction to Mn(II) by sulfite. A similar reduction also occurs on increasing the sulfite concentration as shown in Fig. 1(c). The absorbance increase at 427 nm during the formation of Mn(III) increases linearly with increasing sulfite concentration $(1–10) \times 10^{-5}$ M for 0.10 M Mn(II), 4×10^{-5} M initial Mn(III), 0.5 M N_3^- and pH 6.8), but reaches a limiting value at 2.5×10^{-4} M sulfite presumably due to the interference of the subsequent reduction step under such conditions.

The absorbance–time traces revealed another very interesting complication depending on the selected Mn(II) and sulfite concentrations. Under certain conditions the absorbance increase due to the formation of Mn(III) exhibited a characteristic shoulder, its magnitude depending on the selected conditions. A few typical examples are given in Fig. 2. As the sulfite concentration is increased or the Mn(II) concentration is reduced (all reactions were performed at the same pH, initial Mn(III), azide and oxygen (saturated) concentrations), the initial small shoulder becomes a complete reaction step consisting of a build up and decrease in Mn(III) concentration. It should be emphasized that the observed traces are highly reproducible and not due to some instrument effect. As the sulfite concentration is increased (compare Fig. 2(a)–(c) with (d)–(f)), the shoulder in the trace becomes a peak. In addition, the increased sulfite concentration causes a complete reduction of Mn(III) at low Mn(II) concentrations. At higher Mn(II) concentrations the peak is followed by a subsequent formation of Mn(III) and a final reduction to Mn(II). This sequence can nicely be seen from the series of traces reported in Fig. 3, and also occurs at lower Mn(II) concentrations but only in the presence of low sulfite concentrations. It follows that under certain experimental conditions the sulfite induced autoxidation of Mn(II) to Mn(III) exhibits two reaction cycles.

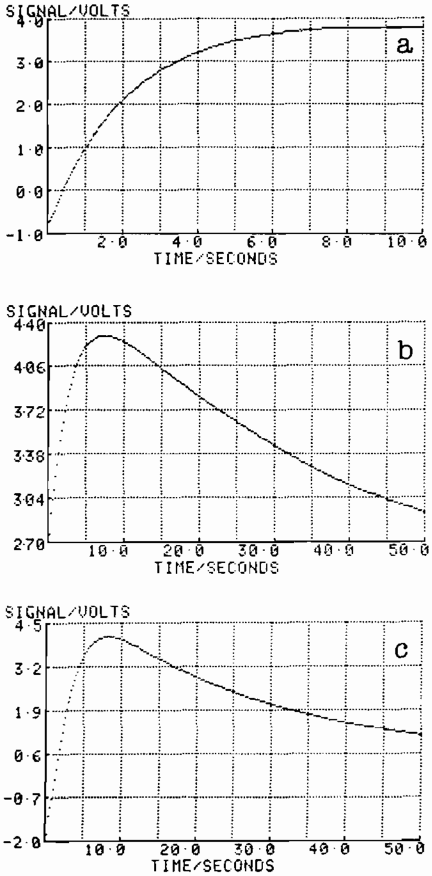

Fig. 1. Typical absorbance–time plots recorded during the sulfite-induced autoxidation of Mn(II) in aqueous azide medium. Conditions: $[Mn(III)]_i = 4 \times 10^{-5}$ M; $[N_3^-] = 0.50$ M; $[HN_3] = 0.005$ M; pH = 6.8; ionic strength = 1.0 M; $[O_2] \approx 8 \times 10^{-4}$ M; temperature = 25.0 °C. a, [Mn(II)] = 0.10 M; $[S(IV)] = 1.0 \times 10^{-4}$ M. b, [Mn(II)] = 0.05 M; $[S(IV)] = 1.0 \times 10^{-4}$ M. c, [Mn(II)] = 0.10 M; $[S(IV)] = 2.0 \times 10^{-4}$ M.

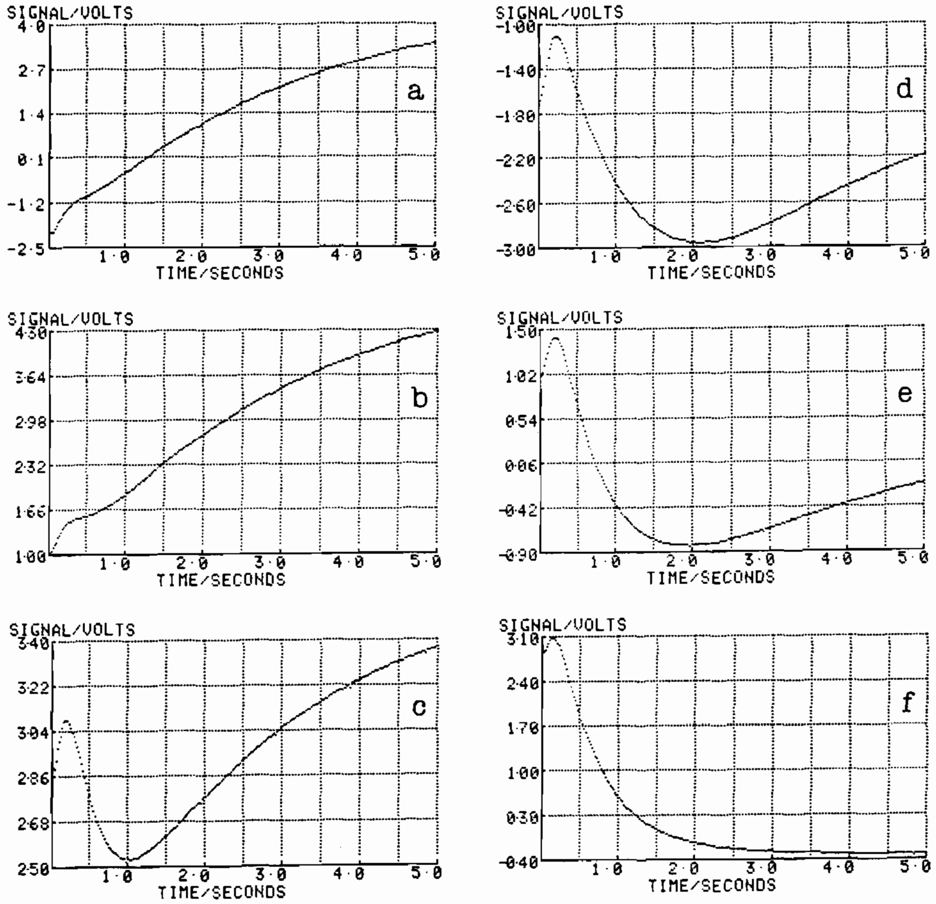

Fig. 2. Typical absorbance–time plots to demonstrate the occurrence of two reaction cycles during the reaction of Mn(II/III) with sulfite in aqueous medium. Conditions: $[\mathrm{Mn(III)}]_i = 4\times10^{-5}$ M; $[\mathrm{N_3^-}] = 0.50$ M; $[\mathrm{HN_3}] = 0.005$ M; pH = 6.8; ionic strength = 1.0 M; $[\mathrm{O_2}] \approx 8\times10^{-4}$ M; temperature = 25.0 °C. a, [Mn(II)] = 0.10 M; $[\mathrm{S(IV)}] = 2.0\times10^{-4}$ M. b, [Mn(II)] = 0.075 M; $[\mathrm{S(IV)}] = 2.0\times10^{-4}$ M. c, [Mn(II)] = 0.050 M; $[\mathrm{S(IV)}] = 2.0\times10^{-4}$ M. d, [Mn(II)] = 0.10 M; $[\mathrm{S(IV)}] = 3.0\times10^{-4}$ M. e, [Mn(II)] = 0.075 M; $[\mathrm{S(IV)}] = 3.0\times10^{-4}$ M. f, [Mn(II)] = 0.050 M; $[\mathrm{S(IV)}] = 3.0\times10^{-4}$ M.

The observed reactions strongly depend on the presence of dissolved oxygen. In the absence of oxygen, addition of sulfite to the Mn(II)/Mn(III) azide solution only results in the reduction of Mn(III) to Mn(II). The experiments reported in Figs. 1–3 were all performed at a saturated oxygen concentration of *c.* 8–10^{-4} M. Under those conditions, sulfite induces the formation of Mn(III) and causes the subsequent reduction (in either one or two cycles) depending on the employed Mn(II) and sulfite concentrations. At lower oxygen concentration (4×10^{-4} M) the occurrence of two cycles is not observed anymore and the formation of Mn(III) is followed by its reduction at high enough sulfite concentrations. It follows that a fine balance between the selected oxygen, sulfite and manganese concentrations determines the reaction sequence and product distribution.

A number of experiments were performed to study the reduction of Mn(III) by sulfite. For this purpose high sulfite concentrations were selected, viz. 4×10^{-3} M, such that the main reaction is the reduction step (similar to that observed in Fig. 2(f)) under such conditions. This reaction does not follow clean first-order kinetics and the absorbance–time traces indicate two consecutive steps of which the rate constants differ by a factor less than two. The process may involve different $\mathrm{Mn^{III}(N_3)(SO_3)}$ complexes, of which the composition is presently unknown, that could account for this effect. Although a detailed kinetic study of this process was not performed, the order of magnitude of the observed rate constants indicated that the reduction of Mn(III) by sulfite is *c.* three times faster than the corresponding reduction of Co(III) under similar experimental conditions [12].

Overall mechanism

The observations reported above clearly demonstrate that the sulfite induced autoxidation of Mn(II) is catalyzed autocatalytically by Mn(III). This catalytic effect plays an important role such that almost no

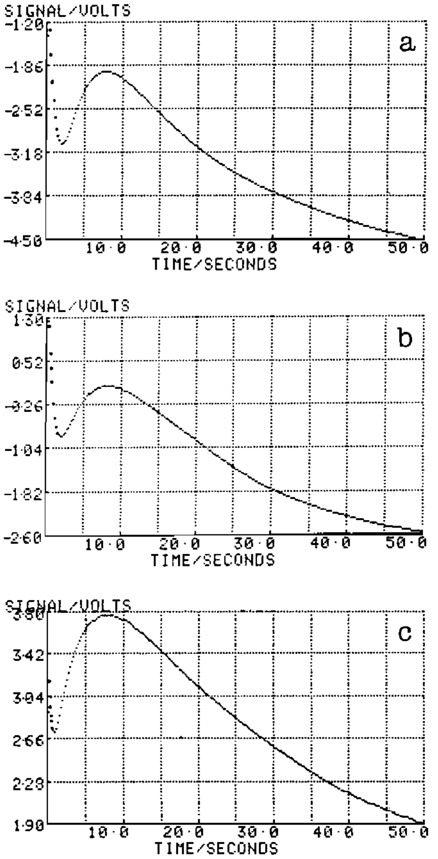

Fig. 3. Typical absorbance-time plots to demonstrate the decomposition of Mn(III) in the presence of sulfite over long reaction times. Conditions: $[\mathrm{Mn(III)}]_i = 4\times10^{-5}$ M; $[N_3^-] = 0.50$ M; $[HN_3] = 0.005$ M; pH = 6.8; ionic strength = 1.0 M; $[O_2] \approx 8\times10^{-4}$ M; temperature = 25 °C. a, [Mn(II)] = 0.10 M; $[\mathrm{S(IV)}] = 3.0\times10^{-4}$ M. b, [Mn(II)] = 0.075 M; $[\mathrm{S(IV)}] = 3.0\times10^{-4}$ M. c, [Mn(II)] = 0.050 M; $[\mathrm{S(IV)}] = 2.0\times10^{-4}$ M.

sulfite-induced autoxidation is observed in the absence of initially added Mn(III). Along the lines of that suggested for the corresponding cobalt system [12], the overall mechanism is summarized in Scheme 1. The reaction sequence is initiated by the reduction of Mn(III) by sulfite during which the sulfite radical SO_3^- is produced. This species now rapidly reacts with dissolved oxygen to produce the SO_5^- radical, which is a powerful oxidant and oxidizes Mn(II) in two consecutive steps. The process also involves the participation of HSO_5^- (peroxomonosulfate, the pK_a of H_2SO_5 is 9.4 [18]) that results in a net production of Mn(III) at low sulfite concentration. During the overall autoxidation process, Mn(II) and sulfite are simultaneously oxidized to Mn(III) and mainly sulfate.

The reaction sequence can account for all observations reported in Figs. 1 to 3. At low sulfite concentration a net production of Mn(III) occurs.

Autocatalysis

$$\mathrm{M(III)} + SO_3^{2-} \longrightarrow \mathrm{M(II)} + SO_3^- \qquad \text{slow}$$

$$SO_3^- + O_2 \longrightarrow SO_5^-$$

$$SO_5^- + \mathrm{M(II)} \xrightarrow{H^+} \mathrm{M(III)} + HSO_5^-$$

$$HSO_5^- + \mathrm{M(II)} \longrightarrow \mathrm{M(III)} + SO_4^{2-} + OH$$

$$\text{or } HSO_5^- + \mathrm{M(II)} \longrightarrow \mathrm{M(III)} + SO_4^- + OH^- \qquad \text{–fast}$$

$$SO_4^- + \mathrm{M(II)} \longrightarrow \mathrm{M(III)} + SO_4^{2-}$$

$$SO_5^- + SO_3^{2-} \xrightarrow{H^+} HSO_5^- + SO_3^-$$

$$\text{and} \longrightarrow SO_4^{2-} + SO_4^-$$

$$SO_3^{2-} + OH \longrightarrow SO_3^- + OH^-$$

Product formation/termination

$$HSO_5^- + SO_3^{2-} \longrightarrow 2SO_4^{2-} + H^+$$

$$SO_3^- + SO_3^- \longrightarrow S_2O_6^{2-}$$

$$SO_4^- + SO_4^- \longrightarrow S_2O_8^{2-}$$

$$SO_5^- + SO_5^- \longrightarrow S_2O_6^{2-} + 2O_2$$

$$\text{or} \longrightarrow S_2O_8^{2} \; + O_2$$

$$SO_5^- + SO_3^- \longrightarrow S_2O_6^{2-} + O_2$$

$$SO_4^- + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^-$$

etc.

Scheme 1. Suggested mechanism. $M = Mn\text{–}N_3$ complex.

On increasing the sulfite concentration, the reduction of Mn(III) becomes more important. Although the produced sulfite radicals should react with O_2 to produce SO_5^- which then reacts with Mn(II), this process strongly depends on the oxygen and Mn(II) concentrations. Thus a build up of Mn(III) can be followed by a reduction by sulfite when the O_2 concentration decreases, which can subsequently result in an increase in Mn(III) concentration when more SO_3^-, i.e. SO_5^-, is produced during the reduction of Mn(III). It follows that the concentrations of O_2, S(IV) and Mn(II) control the overall build up or reduction of Mn(III). At constant O_2 and Mn(II) concentration, sulfite will induce the autoxidation of Mn(II) at low sulfite concentrations, but will cause the reduction of Mn(III) at high sulfite concentrations. An essential aspect is the selected experimental conditions where the concentrations of O_2, sulfite and Mn(III) are of the same order of magnitude. The results in Fig. 2 demonstrate that the produced Mn(III) is less redox sensitive at higher Mn(II) concentrations. This is in agreement with the fact that the redox potential of Mn(III) will decrease with increasing Mn(II) concentration [15], such that the reduction by sulfite becomes less favourable.

We conclude that the Mn(II)/Mn(III)/S(IV)/O_2 system exhibits remarkable properties in terms of metal-catalyzed oxidation of S(IV) and S(IV)-induced oxidation of Mn(II). The crucial reaction in the redox cycle is the reduction of Mn(III) by sulfite, which forms the key step in atmospheric oxidation processes [1–4]. The employment of azide as a ligand assists the stabilization of reactive intermediates and the elucidation of the underlying reaction mechanism. The results of this study throw light on the synergistic effect of manganese in many redox cycles, an aspect that will be treated in more detail in a forthcoming report [13].

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