

# Kinetic Evidence for the Redox Cycling of Manganese(II,III) in the Presence of ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$ in Aqueous Media

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Redox cycling of  $\text{Mn}^{\text{III}}$  in the presence of  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$  in the absence and presence of oxygen was studied by following the increase and decrease of  $\text{Mn}^{\text{III}}$  spectrophotometrically as a function of  $[{}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}]$ ,  $[\text{Mn}^{\text{III}}]$ ,  $[\text{Mn}^{\text{II}}]$  and pH. The autoxidation reaction exhibits typical autocatalytic behaviour in which the induction period depends on the concentrations of  $\text{Mn}^{\text{II}}$  and  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$ . Under acidic conditions the reaction does not take place in the absence of  $\text{Mn}^{\text{II}}$  or  $\text{O}_2$ . The concentrations of  $\text{O}_2$ ,  $\text{Mn}^{\text{II}}$  and  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$  determine whether only oxidation of  $\text{Mn}^{\text{II}}$  to  $\text{Mn}^{\text{III}}$ , or reduction of  $\text{Mn}^{\text{III}}$  to  $\text{Mn}^{\text{II}}$ , or both in one or two redox cycles is observed. Preliminary simulations of some of the observed kinetic traces are presented.

Metal-catalysed oxidation reactions of  $\text{SO}_2$  and  $\text{NO}_x$  species in aqueous solution have attracted the attention of chemists from a variety of disciplines<sup>1–14</sup> due to the importance of such processes both in the atmosphere and in wet limestone flue-gas desulfurization (FGD) systems. A series of studies on the catalytic effect of metal ions and complexes of Fe,<sup>15–19</sup> Co<sup>20</sup> and Mn<sup>21</sup> revealed that the metal-catalysed autoxidation of sulfite and the sulfite-induced autoxidation of the different metal ions can be explained by a common mechanism. In this the trivalent metal ion is reduced by sulfite to produce a sulfite radical which initiates the formation of sulfate and peroxomonosulfate radicals in the presence of  $\text{O}_2$ . These radicals are responsible for the reoxidation of the metal ion to the trivalent state in order to complete the catalytic cycle.<sup>22</sup>

Our current interest concerns the redox behaviour of manganese in the presence of nitrogen–sulfur compounds, which are formed in FGD systems *via* the key compound  $\text{HON}(\text{SO}_3)_2^{2-}$ . The latter is formed in solution *via* the reaction of nitrite with sulfite<sup>23–26</sup> or NO with  $\text{HSO}_3^-$  in the presence of  $\text{Fe}^{\text{II}}$  according to a Boedeker-type mechanism.<sup>27,28</sup> Under acidic conditions,  $\text{HON}(\text{SO}_3)_2^{2-}$  is unstable and decomposes to  $\text{HONH}(\text{SO}_3)^-$ . The dianion  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$  can be formed in FGD systems *via* base hydrolysis of  $\text{HONH}(\text{SO}_3)^-$ ,<sup>29</sup> its reaction with  $\text{NO}_2^-$ ,<sup>30</sup> or the reaction of NO with sulfur(IV) oxides.<sup>31</sup>

In a recent kinetic study of the reduction of  $\text{Mn}^{\text{III}}$  by a variety of nitrogen–sulfur compounds<sup>26</sup> we showed that the results could account for some typical observations made in FGD systems. Limited information on the influence of such compounds on the possible oxidation of divalent metal ions has appeared in the literature. In a study on the reaction of chelated iron(II) nitrosyl complexes with sulfite and hydrogensulfite ions, Littlejohn and Chang<sup>32</sup> reported a mechanism for this reaction which involves the oxidation of  $\text{Fe}^{\text{II}}\text{L}$  [L = a poly(amino-carboxylate)] by  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$ . In much the same way as our earlier study the sulfite-induced autoxidation of  $\text{Mn}^{\text{II}}$  in azide medium,<sup>21</sup> we have now made a systematic kinetic analysis of the possible oxidation of  $\text{Mn}^{\text{II}}$  by  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$  in basic and acidic solutions. We report for the first time kinetic evidence for the redox cycling of  $\text{Mn}^{\text{II}}$  and  $\text{Mn}^{\text{III}}$  in the presence of this dianion.

## Experimental

All reagents were of analytical grade (Merck and Fluka) and deionized water was used to prepare all the solutions. Argon was used to deaerate the solutions where required. The dianion  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$  was synthesized according to a literature procedure.<sup>33</sup> For measurements at high pH a carbonate buffer (0.025 mol  $\text{dm}^{-3}$ ) was used to stabilize the solution pH. Eluents for the ion chromatographic analysis were prepared from sodium carbonate, tetrabutylammonium hydroxide and acetonitrile. The equipment used for this analysis and the selected experimental conditions under which it was performed were the same as those adopted before.<sup>34</sup> The UV/VIS spectra were recorded at constant time intervals on Hewlett-Packard 8452A diode-array and Cary spectrophotometers. These instruments were also used for kinetic measurements of slow reactions in their thermostatted ( $\pm 0.1^\circ\text{C}$ ) cell compartments. Fast reactions were followed on a Durrum D110 stopped-flow instrument. The instruments were run on-line with an IBM compatible personal computer, and the absorbance *vs.* time traces obtained from the OLIS KINFIT (OLIS Inc., Bogart, GA) set of programs were converted into a standard graphical format. The pH measurements were performed on a Metrohm 632 pH-meter equipped with a Sigma glass electrode.

## Results and Discussion

The rate of spontaneous hydrolysis of  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$ <sup>35–37</sup> is plotted as a function of  $[\text{H}^+]$  in Fig. 1, from which it can be seen

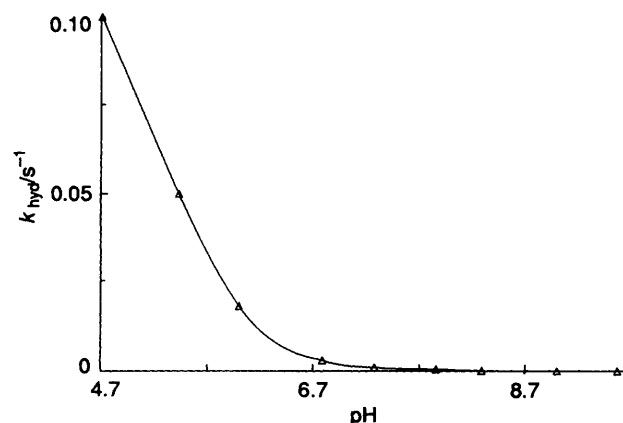
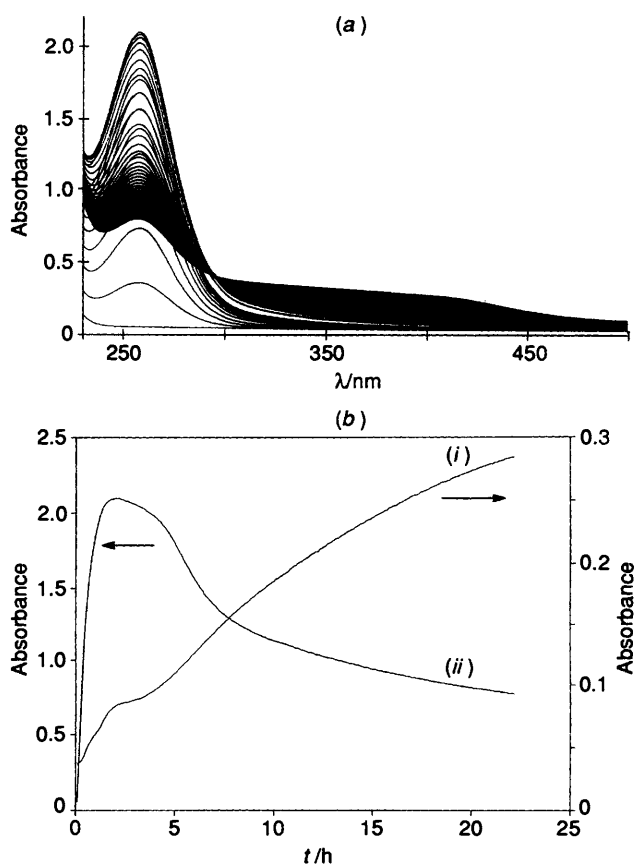
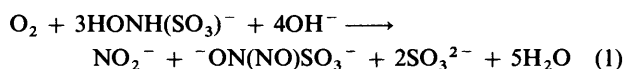


Fig. 1 The pH dependence of the rate of hydrolysis of  ${}^{-}\text{ON}(\text{NO})\text{SO}_3{}^{-}$

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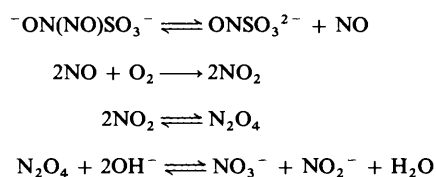
that the dianion is relatively stable in basic solution. On the other hand,  $\text{Mn}^{\text{II}}$  is readily oxidized by dissolved  $\text{O}_2$  in basic solution.<sup>38</sup> Thus a typical experiment at high pH was executed by filling a tandem cuvette (under argon when required) with a deaerated solution of  $\text{Mn}^{\text{II}}$  at neutral pH and a buffered solution containing the dianion. Flue-gas desulfurization systems are generally operated at  $\text{pH} < 7$  and it was therefore of interest to study the reaction at low pH as well. At  $\text{pH} < 7$  both  $^-\text{ON}(\text{NO})\text{SO}_3^-$  and  $\text{Mn}^{\text{III}}$  are unstable. Based on our previous experience in azide media<sup>21</sup> and since the azide ion forms stable complexes with metal ions,<sup>39,40</sup> we stabilized  $\text{Mn}^{\text{III}}$  in this pH range by working in an azide medium. The  $^-\text{ON}(\text{NO})\text{SO}_3^-$  solutions were kept between pH 8 and 9 and were used immediately after preparation.

The first evidence for the oxidation of  $\text{Mn}^{\text{II}}$  by  $^-\text{ON}(\text{NO})\text{SO}_3^-$  was obtained when the possible influence of  $\text{HONH}(\text{SO}_3)^-$  on the autoxidation of  $\text{Mn}^{\text{II}}$  at  $\text{pH} > 10.5$  was studied. Under these conditions no azide was added to stabilize  $\text{Mn}^{\text{III}}$ . When  $\text{HONH}(\text{SO}_3)^-$  is placed in an oxygen-saturated solution buffered at pH 10.5 and immediately mixed with a solution containing  $\text{Mn}^{\text{II}}$  a build-up of a product having  $\lambda_{\text{max}} = 260 \text{ nm}$  is observed, after which  $\text{Mn}^{\text{III}}$  is formed ( $\lambda_{\text{max}} = 400 \text{ nm}$ ) (Fig. 2). The product having  $\lambda_{\text{max}} = 260 \text{ nm}$  is  $^-\text{ON}(\text{NO})\text{SO}_3^-$ , since it is known that  $\text{HONH}(\text{SO}_3)^-$  undergoes base hydrolysis in the presence of oxygen<sup>29</sup> according to equation (1) as illustrated in Fig. 3.

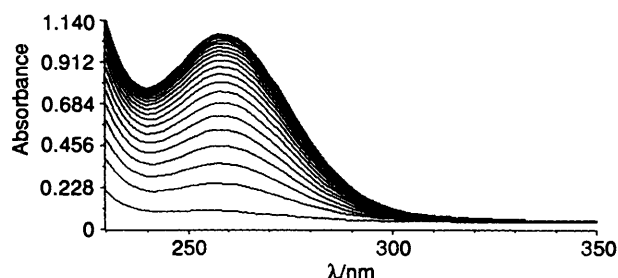


**Fig. 2** (a) Spectral changes during the reaction of  $\text{HONH}(\text{SO}_3)^-$  with  $\text{Mn}^{\text{II}}$ . Conditions:  $[\text{Mn}^{\text{II}}] = 1 \times 10^{-4}$ ,  $[\text{HONH}(\text{SO}_3)^-] = 1 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ; pH 10.5; 25 °C;  $[\text{O}_2] \approx 6.25 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ;  $\Delta t = 360 \text{ s}$  (first 10 spectra) and 1800 s (eleventh and subsequent spectra). (b) Absorbance vs. time traces at different wavelengths, i.e.  $\lambda = 260 \text{ nm}$  (i) where the formation of  $^-\text{ON}(\text{NO})\text{SO}_3^-$  can be observed and 400 nm (ii) where the formation of  $\text{Mn}^{\text{III}}$  can be observed

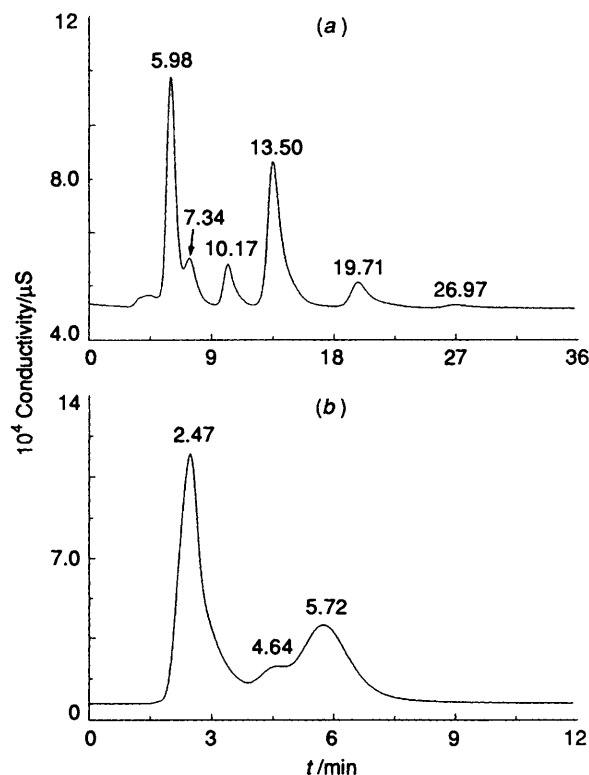
The dianion has an absorption coefficient of 7000  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  at 260 nm.<sup>29</sup> It could also be identified *via* ion chromatographic analysis of the hydrolysis products (Fig. 4). In agreement with a literature finding,<sup>29</sup> the ion chromatographic analysis also confirms the formation of  $\text{NO}_2^-$ ,  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . From Fig. 4 it is clear that  $\text{NO}_3^-$  and  $\text{HON}(\text{SO}_3)_2^{2-}$  are also produced during the base hydrolysis of  $\text{HONH}(\text{SO}_3)^-$ . The formation of  $\text{NO}_3^-$  was accounted for in the initial net reaction,<sup>29</sup> but not in the overall reaction stoichiometry. We suggest that it can be formed according to Scheme 1.



Scheme 1



**Fig. 3** Spectral changes during the base hydrolysis of  $\text{HONH}(\text{SO}_3)^-$ . Conditions:  $[\text{HONH}(\text{SO}_3)^-] = 1 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ; pH 10.5; 25 °C;  $[\text{O}_2] \approx 6.25 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ;  $\Delta t = 3600 \text{ s}$



**Fig. 4** Chromatograms of the products formed during the base hydrolysis of  $\text{HONH}(\text{SO}_3)^-$ . Conditions: pH 10.5; 25 °C;  $[\text{HONH}(\text{SO}_3)^-] = 1 \times 10^{-3}$  mol  $\text{dm}^{-3}$ . (a) Obtained after 24 h of mixing, by ion permeation chromatography (IPC):  $t = 5.98$ ,  $\text{HONH}(\text{SO}_3)^-$ ,  $\text{Cl}^-$ ; 7.34,  $\text{NO}_2^-$ ; 10.17,  $\text{NO}_3^-$ ; 13.5,  $\text{SO}_4^{2-}$ ; 19.71,  $\text{HON}(\text{SO}_3)_2^{2-}$ ; 26.97 s,  $^-\text{ON}(\text{NO})\text{SO}_3^-$ . (b) Obtained after 3 h of mixing by IC:  $t = 2.47$ ,  $\text{HONH}(\text{SO}_3)^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ; 4.64 s,  $\text{SO}_3^{2-}$ ; 5.72 s,  $\text{SO}_4^{2-}$

Further support for oxygen consumption during reaction (1) was obtained by monitoring the concentration of dissolved oxygen with an oxygen-sensitive electrode (OXYTEC) during the course of the reaction.<sup>41</sup> It was found that the concentration decreased according to a first-order decay during the base-hydrolysis reaction.

The formation of  $\text{HON}(\text{SO}_3)_2^{2-}$  in Fig. 4 is ascribed to the reaction of  $\text{NO}_2^-$  with  $\text{SO}_3^{2-}$ . It is expected that the rate of this reaction is slow,<sup>30,42,43</sup> and at high pH it becomes unfavourable compared to the oxidation of  $\text{SO}_3^{2-}$  by dissolved oxygen.

The increase in absorbance at 400 nm in Fig. 2(a) is ascribed to the formation of  $\text{Mn}^{\text{III}}$ . Acidification of such a solution with  $\text{HClO}_4$  caused an immediate shift in the maximum to 460 nm, which is the characteristic absorption of aquated  $\text{Mn}^{\text{III}}$  in acidic solution.<sup>44</sup> The difference in these maxima is ascribed to the hydrolysis of  $\text{Mn}^{\text{III}}$  at pH 10.5 as compared to the hexaqua species in acidic media. The exact nature of the hydrolysed manganese(III) species under our conditions is difficult to predict,<sup>45</sup> and could include  $\text{Mn}(\text{OH})_3$ ,  $\text{MnO}(\text{OH})$ , etc.

The build-up of  $\text{Mn}^{\text{III}}$  is preceded by an induction period during which  $^-\text{ON}(\text{NO})\text{SO}_3^-$  is formed in solution ( $\lambda = 260$  nm) and partial oxidation of  $\text{Mn}^{\text{II}}$  occurs. The dianion then decomposes in two steps of which the second coincides with the formation of  $\text{Mn}^{\text{III}}$  [Fig. 2(b)]. The first part of this decomposition reaction can only be attributed to a concurrent formation and decomposition of the dianion. This hypothesis is further confirmed by the fact that this step coincides with the induction period, before any significant concentration of  $\text{Mn}^{\text{III}}$  is formed in solution. Noteworthy is the isosbestic point at  $\lambda = 296$  nm which suggests a single reaction step between the dianion and  $\text{Mn}^{\text{II}}$  resulting in the formation of  $\text{Mn}^{\text{III}}$ . Ion chromatographic analysis of the products (Fig. 5) formed during this reaction indicated that sulfite, sulfate,  $\text{HON}(\text{SO}_3)_2^{2-}$  and  $\text{NO}_3^-$  were formed. In contrast to the base hydrolysis of  $\text{HONH}(\text{SO}_3)^-$ , no  $\text{NO}_2^-$  could be detected. Its absence in the presence of  $\text{Mn}^{\text{II}}$  can be explained in two ways. First, oxidation of  $\text{NO}_2^-$  by  $\text{Mn}^{\text{III}}$ ,<sup>46</sup> formed due to the  $\text{O}_2$  and  $^-\text{ON}(\text{NO})\text{SO}_3^-$ -induced oxidation of  $\text{Mn}^{\text{II}}$ ,<sup>39</sup> cannot be ruled out. Secondly, it is also possible that, much in the same way as for the oxidation of iron(II) complexes by  $\text{NO}_2^-$ ,<sup>28</sup> a  $\text{Mn}^{\text{II}}-^-\text{ON}(\text{NO})\text{SO}_3^-$  complex can be formed\*<sup>11</sup> (see further Discussion) which reacts with  $\text{NO}_2^-$ . This could result in the formation of  $\text{Mn}^{\text{III}}-^-\text{ON}(\text{NO})\text{SO}_3^-$  and  $\text{NO}$ . The latter can participate in further reactions with  $\text{Mn}^{\text{II}}-^-\text{ON}(\text{NO})\text{SO}_3^-$  and  $\text{O}_2$  to produce  $[\text{Mn}^{\text{II}}\{\text{ON}(\text{NO})\text{SO}_3\}(\text{NO})]$  and  $\text{NO}_2$ , respectively. The  $\text{NO}_2$  can subsequently react with  $\text{Mn}^{\text{II}}$  (ref. 47) to produce  $\text{NO}_2^-$  and  $\text{Mn}^{\text{III}}$ .

These findings are not sufficient evidence to prove that  $^-\text{ON}(\text{NO})\text{SO}_3^-$  oxidizes  $\text{Mn}^{\text{II}}$  to  $\text{Mn}^{\text{III}}$ , since in basic solution the oxidation of  $\text{Mn}^{\text{II}}$  is induced by dissolved oxygen.<sup>38</sup> The reaction of  $\text{HONH}(\text{SO}_3)^-$  with  $\text{Mn}^{\text{II}}$  in the absence of oxygen only results in the formation of different manganese(II) hydroxo species,<sup>38</sup> since  $^-\text{ON}(\text{NO})\text{SO}_3^-$  is only formed from  $\text{HONH}(\text{SO}_3)^-$  in the presence of oxygen.<sup>30,48</sup> It must be kept in mind that the spectral changes reported in Fig. 2 differ completely from those observed for the autoxidation of  $\text{Mn}^{\text{II}}$ .<sup>38</sup> It was therefore necessary to investigate the oxidation of  $\text{Mn}^{\text{II}}$  in the presence of  $^-\text{ON}(\text{NO})\text{SO}_3^-$  under conditions where it does not occur at all when the dianion is not present in solution, i.e. with argon-saturated solutions.

\* Manganese(II) is a  $d^5$  metal ion which causes weak, spin-forbidden, electronic transitions in the UV/VIS region, but due to the absence of crystal-field stabilization energy for this, normally high-spin, ion a weakly bonded complex is expected to be formed. This is also evident from the fact that  $\text{Mn}^{\text{II}}$  does not form strongly bonded complexes with typical ligands as do some of the later first-row transition-metal ions. At high pH hydroxide ligands themselves will be strongly bound and substitution inert, but they may induce a lability of the *trans*-water molecule. Thus the  $[\text{Mn}(\text{H}_2\text{O})_5(\text{OH})]^+$  species is expected to be more substitution labile than is  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ .

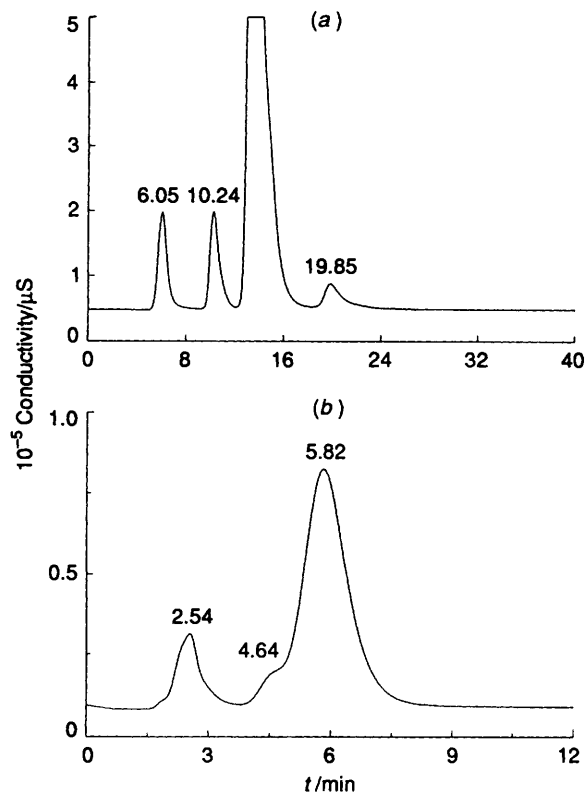


Fig. 5 Chromatograms of the products formed during the reaction of  $\text{HONH}(\text{SO}_3)^-$  with  $\text{Mn}^{\text{II}}$ . Conditions: pH 10.5; 25 °C;  $[\text{HONH}(\text{SO}_3)^-] = 1 \times 10^{-2}$  mol  $\text{dm}^{-3}$ . (a) Obtained by IPC:  $t = 6.05$  s,  $\text{HONH}(\text{SO}_3)^-$ ,  $\text{Cl}^-$ ; 10.24 s,  $\text{NO}_3^-$ ; 12–17 s,  $\text{SO}_4^{2-}$ ; 19.85 s,  $\text{HON}(\text{SO}_3)_2^{2-}$ . (b) Obtained by IC:  $t = 2.54$  s,  $\text{HONH}(\text{SO}_3)^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ; 4.64 s,  $\text{SO}_3^{2-}$ ; 5.82 s,  $\text{SO}_4^{2-}$ .

The dianion is unstable at pH 10.5 and hydrolyses to produce  $\text{N}_2\text{O}$  and sulfate.<sup>49</sup> At 25 °C and 0.025 mol  $\text{dm}^{-3}$  ionic strength the rate constant of this decomposition  $k_{\text{dec}}$  was measured as  $1.4 \times 10^{-4}$   $\text{s}^{-1}$ , in good agreement with a previously reported value of  $1.0 \times 10^{-4}$   $\text{s}^{-1}$  at pH 10.3.<sup>49</sup> Spectral changes upon mixing  $^-\text{ON}(\text{NO})\text{SO}_3^-$  with  $\text{Mn}^{\text{II}}$  in the absence of oxygen are illustrated in Fig. 6(a). These are very similar to the second part of the spectral changes observed when  $\text{HONH}(\text{SO}_3)^-$  is mixed with  $\text{Mn}^{\text{II}}$  (Fig. 2), which confirms that  $\text{HONH}(\text{SO}_3)^-$  first hydrolyses to  $^-\text{ON}(\text{NO})\text{SO}_3^-$  and then participates in the oxidation of  $\text{Mn}^{\text{II}}$ . The decomposition of  $^-\text{ON}(\text{NO})\text{SO}_3^-$ , or  $\text{Mn}^{\text{II}}-^-\text{ON}(\text{NO})\text{SO}_3^-$ , corresponds to the first part of the absorbance vs. time traces [Fig. 6(b)], since no build-up of  $\text{Mn}^{\text{III}}$  was observed during this interval and it coincides with the induction period. The rate constant was measured as  $3 \times 10^{-4}$   $\text{s}^{-1}$ , which is larger than  $k_{\text{dec}}$  and confirms that the decomposition of  $^-\text{ON}(\text{NO})\text{SO}_3^-$  is accelerated by the presence of manganese(II) hydroxides. In Fig. 6(b) the second part of the absorbance vs. time trace at  $\lambda = 260$  nm corresponds to the redox decomposition of the dianion, since it is accompanied by the formation of  $\text{Mn}^{\text{III}}$  observed at  $\lambda = 400$  nm. Only sulfate was observed in an ion chromatographic analysis of the reaction mixture, which further supports the hydrolysis of the dianion as reported in the literature.<sup>48</sup>

According to reaction (1), base hydrolysis of  $\text{HONH}(\text{SO}_3)^-$  in the presence of oxygen results in the formation of  $^-\text{ON}(\text{NO})\text{SO}_3^-$  and sulfite. We therefore also checked the oxidation of  $\text{Mn}^{\text{II}}$  to  $\text{Mn}^{\text{III}}$  by sulfite in Ar-saturated solution under the conditions of the present investigation. The results in Fig. 7 clearly demonstrate rapid hydrolysis of  $\text{Mn}^{\text{II}}$ , followed by slow conversion of  $\text{Mn}^{\text{II}}$  into  $\text{Mn}^{\text{III}}$  in the presence of sulfite. Literature data suggest the formation of  $[\text{Mn}_2(\text{OH})_3]^+$  under these conditions due to the limited solubility of  $\text{Mn}(\text{OH})_2$ .<sup>38,45</sup> The observed spectral changes for the second part of the process

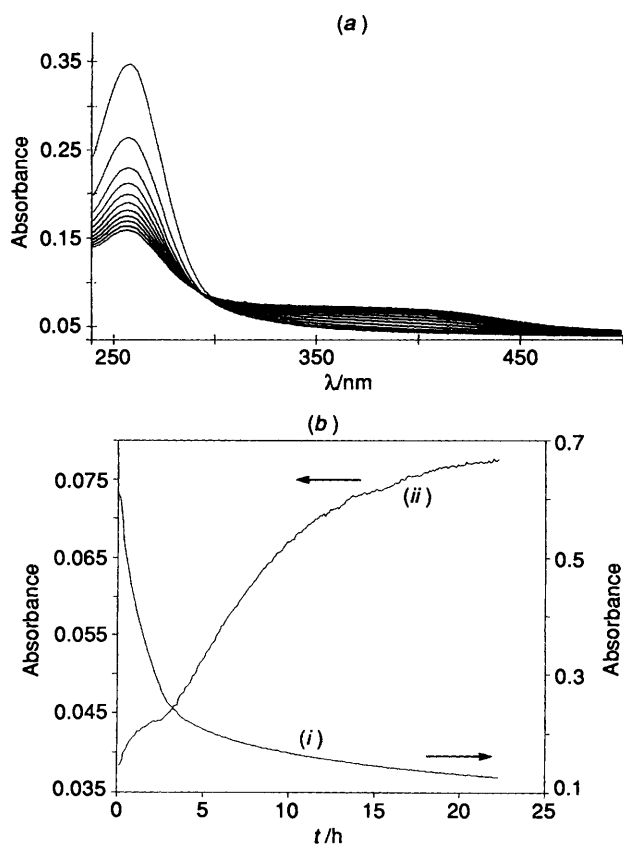


Fig. 6 (a) Spectral changes during the reaction of  $\text{Mn}^{\text{II}}$  with  $\text{ON}(\text{NO})\text{SO}_3^-$ . Conditions:  $[\text{Mn}^{\text{II}}] = 1 \times 10^{-5}$ ,  $[\text{ON}(\text{NO})\text{SO}_3^-] = 1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ; pH 10.5; 25 °C;  $[\text{O}_2] \approx 0$  mol  $\text{dm}^{-3}$ ; between 240 and 500 nm;  $\Delta t = 360$  s. (b) Absorbance vs. time traces at different wavelengths, i.e.,  $\lambda = 260$  nm (i) where a decrease in  $\text{ON}(\text{NO})\text{SO}_3^-$  concentration can be observed and 400 nm (ii) where the formation of  $\text{Mn}^{\text{III}}$  can be observed

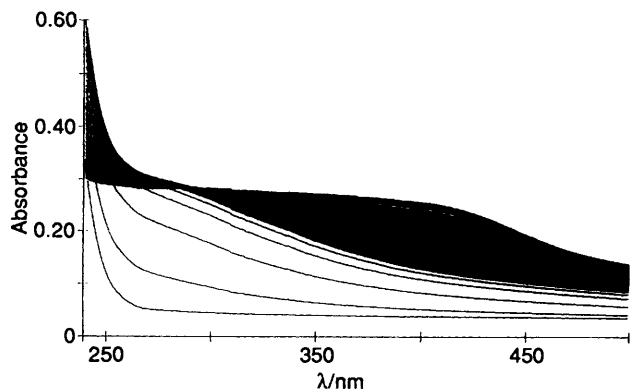


Fig. 7 Spectral changes during the reaction of  $\text{Mn}^{\text{II}}$  with sulfite. Conditions:  $[\text{Mn}^{\text{II}}] = 1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ,  $[\text{S}^{\text{IV}}] = 2$  mmol  $\text{dm}^{-3}$ ; pH 10.5; 25 °C;  $[\text{O}_2] \approx 0$  mol  $\text{dm}^{-3}$

are very similar to those in Fig. 2(a) and can therefore also account for the oxidation of  $\text{Mn}^{\text{II}}$  to  $\text{Mn}^{\text{III}}$ .

Subsequently, a systematic study of the possible oxidation of  $\text{Mn}^{\text{II}}$  by  $\text{ON}(\text{NO})\text{SO}_3^-$ , at pH < 7, and in the presence of low concentrations of  $\text{Mn}^{\text{III}}$  was performed. Azide was used throughout these experiments to stabilize  $\text{Mn}^{\text{III}}$  in this pH range.<sup>21</sup> The UV/VIS spectra and the absorbance vs. time traces [Fig. 8(a) and 8(b)] indicate that upon mixing, complex formation between  $\text{Mn}^{\text{II}}$  and the dianion causes the maximum at 410 nm (due to the presence of  $\text{Mn}^{\text{III}}$ ) to shift to 360 nm, after which  $\text{Mn}^{\text{II}}$  is oxidized to  $\text{Mn}^{\text{III}}$ . Under similar conditions, but in the absence of initially added  $\text{Mn}^{\text{III}}$ , complex formation was

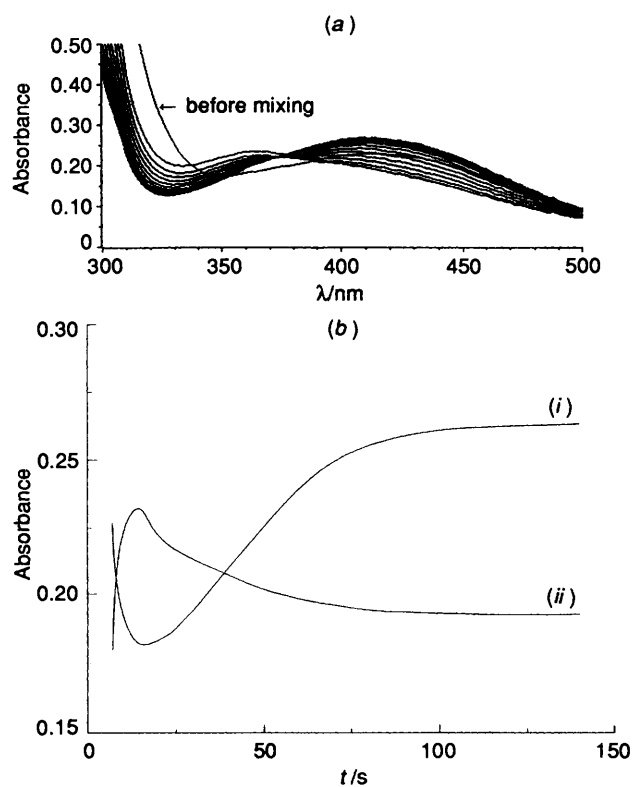


Fig. 8 (a) Spectral changes during the reaction of  $\text{ON}(\text{NO})\text{SO}_3^-$  with  $\text{Mn}^{\text{III}}$ . Conditions:  $[\text{ON}(\text{NO})\text{SO}_3^-] = 4$  mmol  $\text{dm}^{-3}$ ;  $[\text{Mn}^{\text{II}}] = 0.05$  mol  $\text{dm}^{-3}$ ;  $[\text{N}_3^-] = 0.5$  mol  $\text{dm}^{-3}$ ; pH 6; 25 °C;  $I = 0.6$  mol  $\text{dm}^{-3}$ ;  $[\text{O}_2] \approx 6.25 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ;  $[\text{Mn}^{\text{III}}] = 0.05$  mmol  $\text{dm}^{-3}$ ,  $\Delta t = 7$  s. (b) Absorbance vs. time analysis at different wavelengths, i.e.  $\lambda = 360$  nm (i) and 420 nm (ii)

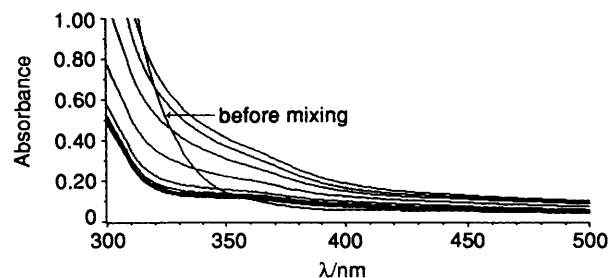


Fig. 9 Spectral changes during the reaction of  $\text{ON}(\text{NO})\text{SO}_3^-$  with  $\text{Mn}^{\text{II}}$ . Conditions:  $[\text{ON}(\text{NO})\text{SO}_3^-] = 4$  mmol  $\text{dm}^{-3}$ ;  $[\text{Mn}^{\text{II}}] = 0.05$  mol  $\text{dm}^{-3}$ ;  $[\text{N}_3^-] = 0.5$  mol  $\text{dm}^{-3}$ ; pH = 6; 25 °C;  $I = 0.6$  mol  $\text{dm}^{-3}$ ;  $[\text{O}_2] \approx 6.25 \times 10^{-4}$  mol  $\text{dm}^{-3}$

again observed at 365 nm but no further oxidation of  $\text{Mn}^{\text{II}}$  could be seen (Fig. 9). The product formed at  $\lambda = 365$  nm most probably is  $\text{Mn}^{\text{II}}-\text{ON}(\text{NO})\text{SO}_3^-$ , since the formation of  $\text{Mn}^{\text{II}}(\text{NO})$  or  $\text{Mn}^{\text{II}}(\text{SO}_3)$  is ruled out by the fact that when the experiment in Fig. 8(a) was repeated with NO or  $\text{SO}_3^{2-}$  as reactant species no oxidation of  $\text{Mn}^{\text{II}}$  in the case of NO or product formation at 365 nm in the case of  $\text{SO}_3^{2-}$  was observed. A series of kinetic measurements revealed no significant influence of the concentration ( $1 \times 10^{-4}$ – $3 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) of  $\text{ON}(\text{NO})\text{SO}_3^-$  on the observed rate constant for the formation of  $\text{Mn}^{\text{III}}$  ( $0.08 \pm 0.01$ – $0.11 \pm 0.01$  s $^{-1}$  at 25 °C, pH 6 and  $[\text{Mn}^{\text{III}}] = 5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ). Under the same conditions, but with a higher  $[\text{Mn}^{\text{III}}]$ , the observed rate constant increases dramatically ( $1.95 \pm 0.06$ – $1.99 \pm 0.01$  s $^{-1}$  at  $[\text{Mn}^{\text{III}}] = 1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ). This confirms that  $\text{Mn}^{\text{III}}$  is the active species during the autocatalytic process.

A detailed quantitative kinetic investigation of the  $\text{ON}(\text{NO})\text{SO}_3^-$ -induced oxidation of  $\text{Mn}^{\text{II}}$  was then performed in which

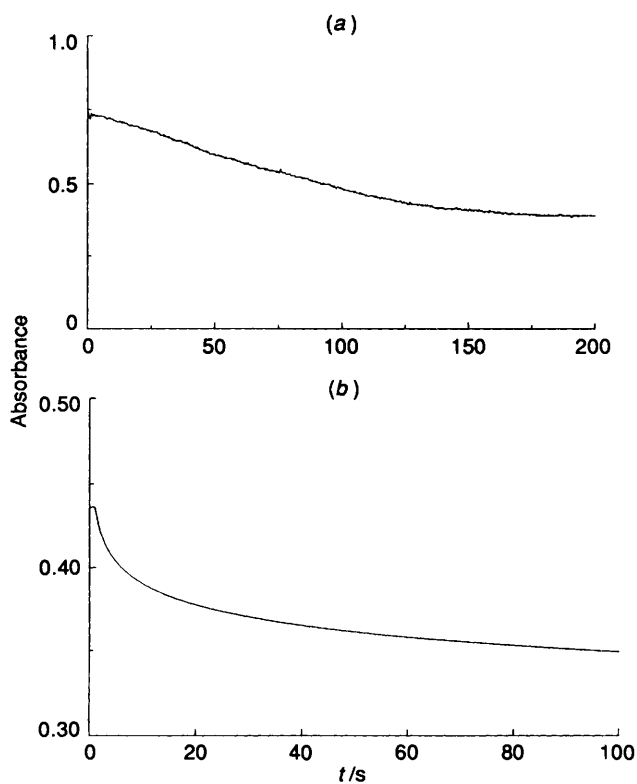


Fig. 10 Absorbance vs. time plots during the reaction of  ${}^-ON(NO)SO_3^-$  with  $Mn^{II/III}$  in the absence of oxygen. Conditions:  $[Mn^{II}] = 0.025$ ,  $[N_3^-] = 0.5 \text{ mol dm}^{-3}$ ,  $[{}^-ON(NO)SO_3^-] = 8 \text{ mmol dm}^{-3}$ ;  $25^\circ\text{C}$ ;  $I = 1.0 \text{ mol dm}^{-3}$ ;  $\lambda = 420 \text{ nm}$ ; pH 6 (a) or 7 (b)

the influence of pH,  $[Mn^{II}]$  and  $[Mn^{III}]$  was studied. In the absence of  $O_2$  only the reduction of  $Mn^{III}(N_3)_2^{2+}$  to  $Mn^{II}$  could be observed [Fig. 10(a) and 10(b)]. The fast and slow reactions in Fig. 10(b) are not so uncommon for the reduction of  $Mn^{III}(N_3)_2^{2+}$  by nitrogen-sulfur oxides. We have reported in detail on the mechanism by which  $Mn^{III}(N_3)_2^{2+}$  is reduced by different nitrogen-sulfur compounds<sup>26</sup> and found similar complications for  $S^{IV}$ ,  $HN(SO_3)_2^{2-}$  and  $ON(SO_3)_3^{3-}$ . The two steps observed were interpreted either in terms of a rate-determining substitution of a  $H_2O$  or  $N_3^-$  ligand on the manganese(III) species followed by a rapid electron-transfer reaction, or by a slow intramolecular electron-transfer reaction following the rapid formation of a manganese(III)-nitrogen-sulfur complex. In the presence of  $O_2$  the absorbance traces look completely different (Fig. 11). An increase in  $[Mn^{III}]$  as a function of time is observed. When the  $[{}^-ON(NO)SO_3^-]$  is low only oxidation of  $Mn^{II}$  to  $Mn^{III}$  can be observed. Upon increasing the  $[{}^-ON(NO)SO_3^-]$ ,  $Mn^{II}$  is first oxidized to  $Mn^{III}$  and then a further build-up of  $Mn^{III}$  is preceded by an induction period. Upon increasing the  $[{}^-ON(NO)SO_3^-]$  further the induction period becomes a complete reaction step consisting of a decrease and increase in  $Mn^{III}$ . When  $[Mn^{II}]$  is lowered the first reduction step can be observed at low dianion concentrations. This step probably consists of simultaneous oxidation and reduction of  $Mn^{II}$  and  $Mn^{III}$ , respectively. Upon increasing  $[Mn^{III}]$  and pH, the complete redox cycle proceeds over a shorter reaction time.

**Suggested Mechanism.**—At high pH the formation of  $HON(SO_3)_2^{2-}$ ,  ${}^-ON(NO)SO_3^-$  and sulfite during the reaction of  $HONH(SO_3)^-$  with  $Mn^{II}$  can be explained in terms of the spontaneous hydrolysis of  $HONH(SO_3)^-$  [reaction (1)] and the Boedeker-type reaction outlined in Scheme 2.<sup>28</sup> The overall reaction results in the oxidation of  $Mn^{II}$  to  $Mn^{III}$  as in Fig. 2. A simulation of the observed kinetic traces is not possible

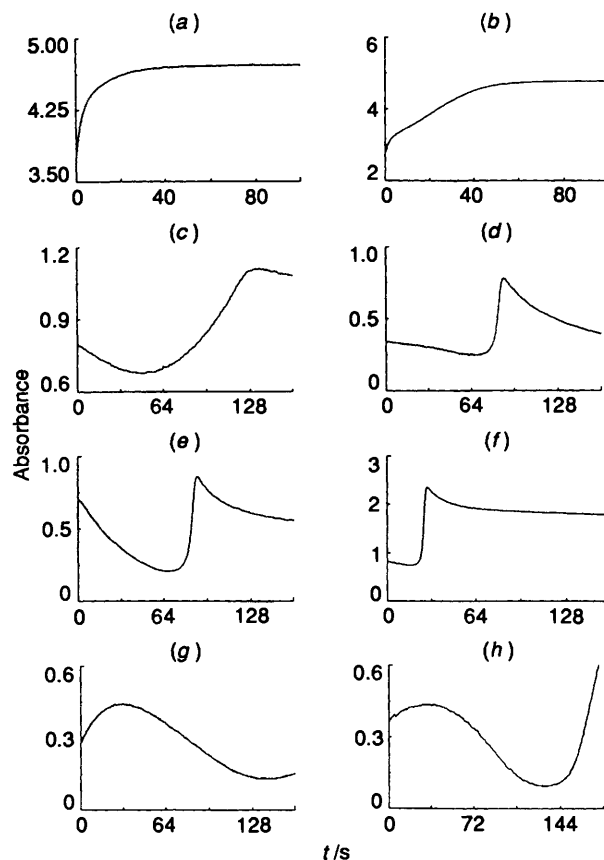
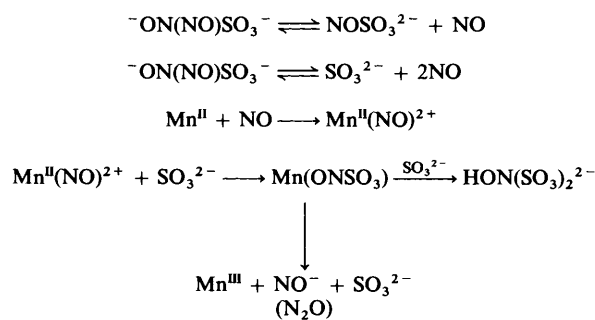


Fig. 11 Typical absorbance vs. time plots to demonstrate the occurrence of two reaction cycles during the reaction of  $Mn^{II/III}$  with  ${}^-ON(NO)SO_3^-$  in aqueous media. Conditions:  $[N_3^-] = 0.5 \text{ mol dm}^{-3}$ ; pH 6 [(a)–(f)] or 7 [(g), (h)];  $I = 1.0 \text{ mol dm}^{-3}$ ;  $[O_2] \approx 6.25 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $25^\circ\text{C}$ ;  $\lambda = 420 \text{ nm}$ ;  $0.1 \text{ mol dm}^{-3}$  [(f)];  $[Mn^{II}] = 0.05$  [(a)–(c)],  $0.025 \text{ mol dm}^{-3}$  [(d)–(h)];  $[Mn^{III}] = 0.05$  [(a)–(e), (g), (h)],  $[{}^-ON(NO)SO_3^-] = 0.2$  [(a)],  $2$  [(b)],  $4$  [(g)],  $6$  [(c), (d), (f), (h)],  $8 \text{ mmol dm}^{-3}$  [(e)]

due to a lack of information on the rate constants of the various reaction steps in Scheme 2 (see further Discussion). Evidence for the formation of  $Mn^{II}(NO)^{2+}$  has been reported.<sup>50</sup>



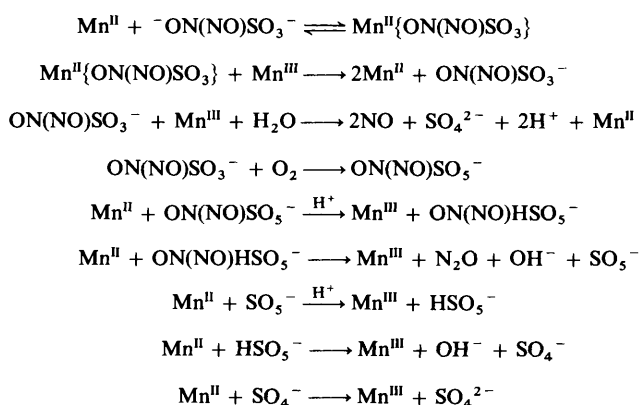
Scheme 2

At low pH in azide media the results indicate that the oxidation of  $Mn^{II}$  to  $Mn^{III}$  is preceded by complex formation between  $Mn^{II}$  and  ${}^-ON(NO)SO_3^-$ . In agreement with our results on the sulfite-induced autooxidation of  $Mn^{II}$ ,<sup>21</sup> as well as those recently published elsewhere,<sup>1</sup> the  ${}^-ON(NO)SO_3^-$ -induced autooxidation of  $Mn^{II}$  is affected autocatalytically by  $Mn^{III}$ , and no significant oxidation is observed in the absence of initially added  $Mn^{III}$ . Based on this result the overall mechanism is suggested to follow the reactions outlined in Scheme 3. This reaction sequence involves very similar steps to those suggested

**Table 1** Suggested mechanism and selected stability and rate constants used for the simulations in Fig. 12

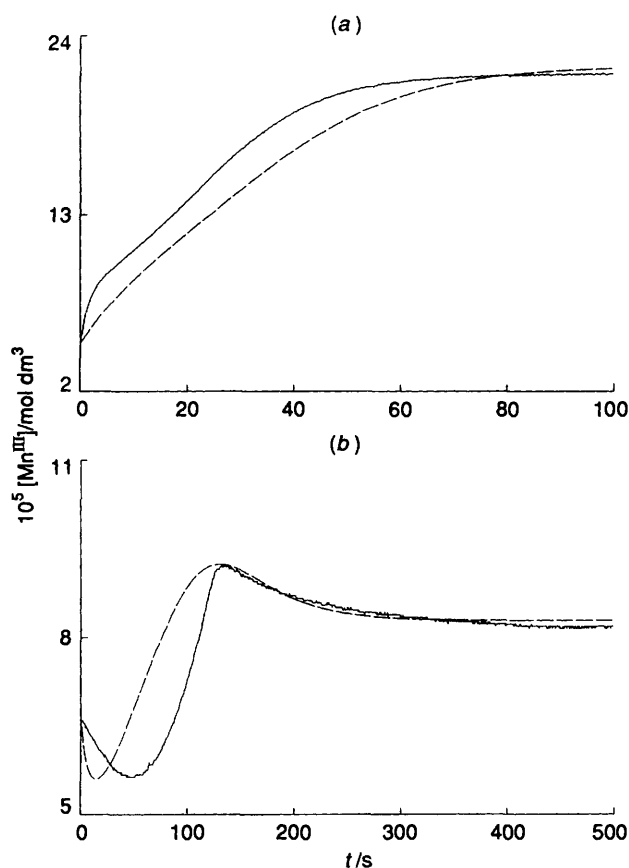
Reaction	Stability or rate constant <sup>a</sup>	
	Lit. value	Value used in simulation
$\text{Mn}^{\text{II}} + ^-\text{ON}(\text{NO})\text{SO}_3^- \rightleftharpoons \text{Mn}^{\text{II}}\{\text{ON}(\text{NO})\text{SO}_3\}$	$2.7 \pm 1.1^{b,c}$	$2.4^c$
$\text{Mn}^{\text{II}}\{\text{ON}(\text{NO})\text{SO}_3\} + \text{Mn}^{\text{III}} \longrightarrow 2\text{Mn}^{\text{II}} + 2\text{NO} + \text{SO}_3^-$	$8 \times 10^{2d}$	$5 \times 10^2$
$\text{Mn}^{\text{III}} + \text{SO}_3^- + \text{H}_2\text{O} \longrightarrow \text{Mn}^{\text{II}} + \text{SO}_4^{2-} + 2\text{H}^+$	$1.5 \times 10^{7e}$	$3.8 \times 10^8$
$\text{SO}_3^- + \text{O}_2 \longrightarrow \text{SO}_5^-$	$(1.1-2.5) \times 10^{9e,f}$	$2.5 \times 10^9$
$\text{Mn}^{\text{II}} + \text{SO}_5^- + \text{H}^+ \longrightarrow \text{Mn}^{\text{III}} + \text{HSO}_5^-$	<i>ca.</i> $10^{8f}$	$5 \times 10^8$
$\text{Mn}^{\text{II}} + \text{HSO}_5^- \longrightarrow \text{Mn}^{\text{III}} + \text{SO}_4^{2-} + \text{OH}^-$	Slow <sup>f</sup>	$< 1 \times 10^4$
$\text{Mn}^{\text{II}} + \text{HSO}_5^- \longrightarrow \text{Mn}^{\text{III}} + \text{SO}_4^{2-} + \text{OH}^-$	Slow <sup>f</sup>	$< 1 \times 10^4$
$\text{Mn}^{\text{II}} + \text{SO}_4^- \longrightarrow \text{Mn}^{\text{III}} + \text{SO}_4^{2-}$	$3 \times 10^{7f}$	$3 \times 10^7$
$\text{Mn}^{\text{II}} + \text{OH}^- + \text{H}^+ \longrightarrow \text{Mn}^{\text{III}} + \text{H}_2\text{O}$	$2.6 \times 10^{7f}$	$2.6 \times 10^7$
$^-\text{ON}(\text{NO})\text{SO}_3^- + \text{H}^+ \longrightarrow \text{HSO}_4^- + \text{N}_2\text{O}$	$2 \times 10^{4g}$	$4 \times 10^4$
$\text{SO}_5^- + \text{SO}_5^- \longrightarrow 2\text{SO}_4^- + \text{O}_2$	$1 \times 10^7 - 1 \times 10^{9e,f}$	$1.1 \times 10^7$
$\text{SO}_5^- + \text{SO}_5^- \longrightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2$	$1.4 \times 10^{8f}$	$5 \times 10^7$
$\text{SO}_3^- + \text{SO}_3^- \longrightarrow \text{S}_2\text{O}_6^{2-}$	$1.8 \times 10^8 - 2.3 \times 10^{9e,f}$	$2.5 \times 10^8$

<sup>a</sup> In units of  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$  unless otherwise stated. <sup>b</sup> Mean value of various complex-formation constants of  $\text{Mn}^{\text{II}}$  reported in ref. 40. <sup>c</sup> In units of  $\text{dm}^3 \text{mol}^{-1}$ . <sup>d</sup> Experimental value measured at pH 6, 25 °C,  $I = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{Mn}^{\text{III}}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$  and  $[\text{N}_3^-]_{\text{T}} = 0.5 \text{ mol dm}^{-3}$ . <sup>e</sup> Data quoted in ref. 51. <sup>f</sup> Data quoted in ref. 1. <sup>g</sup> Data taken from refs. 35-37 and converted into a second-order rate constant for the acid-catalysed reaction.

**Scheme 3**

before to account for the redox cycling of  $\text{Mn}^{\text{II/III}}$  under such conditions in the presence of sulfite and oxygen.<sup>1,21</sup> The difference in the present system is that  $^-\text{ON}(\text{NO})\text{SO}_3^-$  is the species responsible for the redox cycling, and we therefore include the formation of an oxidized  $\text{ON}(\text{NO})\text{SO}_3^-$  species which can react rapidly with molecular oxygen to produce a peroxomonosulfate analogue. This species is presumably a strong oxidant (similar to  $\text{SO}_5^-$ ) and can induce the oxidation of  $\text{Mn}^{\text{II}}$  as shown in the subsequent reactions. It also involves the formation of  $\text{SO}_5^-$  radicals which follows the reaction sequence suggested before.<sup>20,22,51</sup> Scheme 3 can in principle account for a single redox cycle of  $\text{Mn}^{\text{II/III}}$ , in which the initial presence of some  $\text{Mn}^{\text{III}}$  leads to the production of  $\text{ON}(\text{NO})\text{SO}_3^-$  which induces the autoxidation of  $\text{Mn}^{\text{II}}$  in the subsequent reaction steps. The  $^-\text{ON}(\text{NO})\text{SO}_3^-:\text{O}_2$  ratio determines whether oxidation of  $\text{Mn}^{\text{II}}$  or reduction of  $\text{Mn}^{\text{III}}$  will occur, as reported in the case of sulfite.<sup>21</sup> At higher concentrations of  $^-\text{ON}(\text{NO})\text{SO}_3^-$  the reduction to  $\text{Mn}^{\text{II}}$  will be favoured, whereas at lower concentrations an overall oxidation of  $\text{Mn}^{\text{II}}$  will be observed.

The results in Fig. 11 clearly demonstrate that under certain experimental conditions up to two redox cycles are observed. A similar result was observed in the corresponding sulfite system.<sup>21</sup> This is in the present case probably due to two possible redox steps, one between  $\text{Mn}^{\text{III}}$  and  $^-\text{ON}(\text{NO})\text{SO}_3^-$  co-ordinated to  $\text{Mn}^{\text{II}}$  at low  $[\text{Mn}^{\text{III}}]$ , and another directly



**Fig. 12** Simulated (---) kinetic traces based on the mechanism and constants given in Table 1 for the experimental conditions in (a) Fig. 11(b) and (b) Fig. 11(c)

between  $\text{Mn}^{\text{III}}$  and the dianions at higher  $[\text{Mn}^{\text{III}}]$ . Thus, as  $\text{Mn}^{\text{III}}$  is formed during the  $^-\text{ON}(\text{NO})\text{SO}_3^-$ -induced autoxidation of  $\text{Mn}^{\text{II}}$ , the latter reaction can account for the second redox cycle. Alternatively, the reactions in Scheme 3 contain two species which can induce the autoxidation process, *viz.*  $\text{ON}(\text{NO})\text{SO}_5^-$  and  $\text{SO}_5^-$ . It follows that, under particular conditions, the formation of  $\text{SO}_5^-$  (and subsequently  $\text{HSO}_5^-$  and  $\text{SO}_4^-$ ) could account for the second redox cycle of  $\text{Mn}^{\text{II/III}}$ .

We conclude that the general mechanism outlined in Scheme

3 can in principle account qualitatively for the observed kinetic traces. At present not enough information on the various reaction steps is available to allow a more quantitative treatment. If we assume that the intermediate  $\text{ON}(\text{NO})\text{SO}_3^-$  species decomposes spontaneously to  $\text{NO}$  and  $\text{SO}_3^-$ , a modified reaction scheme with more known constants can be derived (see Table 1). Simulations on the basis of this scheme using the ZITA program<sup>52</sup> for some of the experimental conditions of Fig. 11 are reported in Fig. 12. The simulated kinetic traces are in close agreement with those found experimentally, from which it follows that the suggested scheme in Table 1 can in principle account for the type of kinetic traces in Fig. 11. Efforts to simulate the redox cycling of  $\text{Mn}^{\text{II/III}}$  in the presence of  $\text{ON}(\text{NO})\text{SO}_3^-$  and oxygen under other experimental conditions will be continued and more details on these types of reaction mechanisms should be forthcoming.

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