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# Influence of mixed sulfur–nitrogen oxides on the redox kinetics of iron ions in aqueous solution

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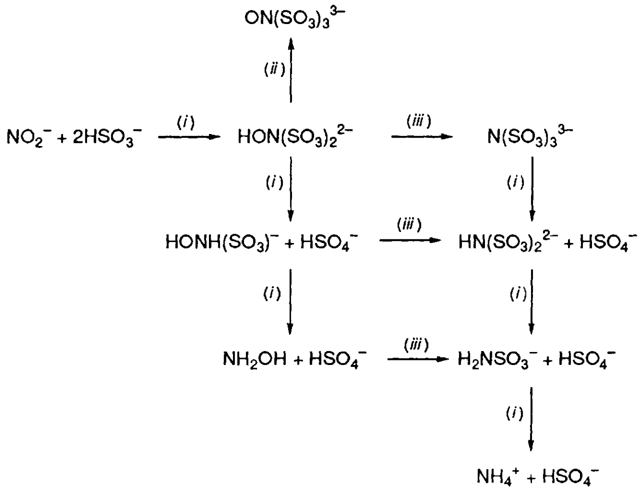
The influence of mixed sulfur–nitrogen oxides on the redox chemistry of iron-(III) and -(II) species in aqueous solution was studied kinetically as a function of various concentrations. Two oxides, *viz.* $HONH(SO_3)^-$ and $HON(SO_3)_2{}^{2-}$, were found to reduce $Fe^{III}$ to $Fe^{II}$, whereby these oxides undergo an iron(III)-induced hydrolysis reaction. The hydrolysis products were analysed by ion chromatography. These redox reactions can in principle account for the inhibiting effect of sulfur–nitrogen oxides on the metal-catalysed autoxidation of sulfur(IV) oxides. Possible reaction mechanisms are suggested.

The environmental importance of mixed sulfur–nitrogen oxides and their eventual influence on atmospheric oxidation processes are not well understood. Further investigations therefore could yield valuable information. Recent studies have shown that such oxides can affect the catalysed autoxidation of sulfur dioxide in flue-gas desulfurization (FGD) systems used in coal-fired power plants.[1,2]

The oxides in question are produced in mixtures of dissolved $SO_2$ and nitrogen-(II) and -(IV) oxides (NO, $NO_2$), in which the conjugate-base ions of the acids formed (*i.e.* $HSO_3{}^-$, $SO_3{}^{2-}$, $NO_2{}^-$), and including metal-complexed NO, undergo a series of reactions. Several mixed sulfur-nitrogen oxides are produced and exhibit a complicated set of reactions (Scheme 1), involving the interaction with sulfite, spontaneous and acid-catalysed hydrolysis and redox reactions, as summarized elsewhere.[3–6] Although the chemistry of sulfur-nitrogen oxides has been studied by a number of groups,[3–9] the development of appropriate analytical techniques[10] should help to clarify further a number of the suggested reaction steps.

In FGD systems $CaCO_3$ which is contaminated by metal impurities (Mn, Fe) is used to precipitate the sulfate produced. The presence of these metal ions favours the metal-catalysed autoxidation of dissolved $SO_2$ to sulfate.[11,12] High concentrations of sulfur–nitrogen oxides are generally found to be associated with an inhibition of the overall oxidation process, which is expressed by a high concentration of dissolved sulfite and a low concentration of precipitated $MnO_2$ in the $CaSO_4$ product. The installation of selective catalysed reduction systems (DENOX systems) for the removal of $NO_x$ from flue gases has changed the chemical processes in those FGD systems, which are deployed after the DENOX systems.[2,13,14] Much lower concentrations of sulfur–nitrogen oxides were found in these systems, whereas the overall oxidation processes are improved (low concentrations of free sulfite, high concentrations of $MnO_2$ precipitates in the gypsum produced). All these observations point to a connection between the concentration level of oxides and the overall oxidation process in FGD systems.

Recent studies in our laboratories have focused on the interaction of a series of sulfur–nitrogen oxides with manganese-(II) and -(III) species in order to clarify the underlying reaction mechanisms and product distribution.[15] The results showed that the oxides are able to reduce $Mn^{III}$ to $Mn^{II}$, whereby these oxides undergo a $Mn^{III}$-induced hydrolysis reaction.[15] These redox reactions can account for the inhibiting effect of the oxides mentioned above since they withdraw from the system the trivalent initiator ions for the metal-induced autoxidation of sulfite.



**Scheme 1** Formation and hydrolysis reactions of nitrogen–sulfur compounds. (*i*) $H^+$, water; (*ii*) oxidation, $HSO_3{}^-$; (*iii*) $HSO_3{}^-$

We have now investigated the interaction of a series of sulfur–nitrogen oxides with iron-(III) and -(II) species in order to establish whether or not iron ionic species react in a comparable way to manganese species. The results show that $HONH(SO_3)^-$ and $HON(SO_3)_2{}^{2-}$ are the principal reactive (SN) species involved in controlling the redox behaviour of iron-(III) and -(II) species in aqueous solution.

## Experimental

Chemicals of analytical reagent grade (Merck, Fluka and Aldrich) and deionized Millipore water were used to prepare all solutions. Argon was used to deaerate solutions when required. Aqueous $HClO_4$, HCl and NaOH were used to adjust the pH, and $NaClO_4$, NaCl, $Na_2SO_4$, $Na(O_2CH)$, $Na(O_2CMe)$ and $NaN_3$ to adjust the ionic strength. The ions $HON(SO_3)_2{}^{2-}$, $HONH(SO_3)^-$, $ON(SO_3)_3{}^{3-}$ and $N(SO_3)_3{}^{3-}$ were synthesized according to literature procedures,[16–19] and their purity was checked by ion chromatography.[10] Eluents for the latter were prepared from sodium carbonate, tetrabutylammonium hydroxide and acetonitrile. Solutions of $Fe^{III}$ were stabilized at pH 5–6 in either an azide or acetate medium. In the former case $NaN_3$ and $HClO_4$, and in the latter case $Na(O_2CMe)$ and $HClO_4$, were used to obtain the desired pH. In addition, a formate buffer (pH 3.6) was also used to investigate the iron(III) system in this pH range.

The UV/VIS spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. Kinetic measurements for slow reactions were performed in the thermostatted cell compartment of the same spectrophotometer or in a Shimadzu UV-250 spectrophotometer. For fast reactions a Durrum D110 stopped-flow spectrophotometer was used. Data fitting was performed with the OLIS KINFIT (Bogart, Georgia) set of programs. Details of the ion-chromatographic procedures and equipment used are given elsewhere.[10] The IR spectra of the gas-phase products of the reaction between iron(III) perchlorate and $HONH(SO_3)^-$ were recorded in a 10 cm gas cuvette on a Nicolet 5 SX FT-IR instrument. The evacuated gas cuvette was used to obtain a sample of the gas-phase species of the reaction when carried out in a sealed flask.

## Results and Discussion

### General considerations and observations

The redox chemistry of iron-(III) and -(II) species in the presence of a number of sulfur–nitrogen oxides has been investigated. The principal objective was to determine whether iron reacts in a similar way to manganese under parallel conditions. The emphasis of the investigation was on iron(III) complexes with weaker co-ordinating anions *e.g.* perchlorate, chloride and sulfate. Both chloride and sulfate are present at high concentrations (several g $l^{-1}$) in the scrubber solutions.[2] The pH range of common FGD systems (4.5–5.5) requires the use of stable iron(III) complexes in order to investigate the interaction of iron species with sulfur–nitrogen oxides in this pH range.

Iron salts in aqueous solution form different aquated species, depending on the pH and concentration. The most important equilibria of the aquated iron(III) ions are (1)–(3). Here the value

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+; \quad K_1 = 6.4 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{(ref. 20)} \quad (1)$$

$$[Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + H^+; \quad K_2 = 3.2 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{(ref. 21)} \quad (2)$$

$$2[Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+} + 2H_2O; \quad K_3 = 44\ \text{dm}^3\ \text{mol}^{-1}\ \text{(ref. 22)} \quad (3)$$

of $K_1$ is given at 25 °C and 0.1 mol $dm^{-3}$ ionic strength, and those for $K_2$ and $K_3$ at 25 °C and zero ionic strength. These equilibria depend on the nature of the anion, since it is well known that anions such as $Cl^-$, $SO_4^{2-}$ and $HCO_2^-$ form stable complexes with aquated iron(III).

Investigations dealing with the substitution behaviour of these complexes have shown that the iron pentaaquahydroxo complex is significantly more labile than the hexaaqua complex,[23–25] due to the *trans* labilization effect of the co-ordinated hydroxy group. The distribution curves (Fig. 1[26]), based on the constants given in equation (1), show the different iron species present as a function of pH. It is evident that in a weakly acidic medium ($2 \leqslant pH \leqslant 4$) four different iron species are present at varying concentrations. At pH *ca.* 3 and a total iron concentration of $10^{-4}$ mol $dm^{-3}$ the iron(III) solutions become pale yellow since the iron hydroxo species dominate under such conditions. With increasing pH ($> 3$) the solutions become turbid, due to the formation of higher iron hydroxo species (dimers and polymers), and therefore a spectrophotometric investigation of these solutions is precluded. Hence it was necessary to stabilize iron(III) with complexing reagents. Based on our earlier experience,[15] we used an azide and an acetate medium to stabilize iron(III) at a higher pH (5–6). A formate buffer was used at pH 3.6.

The chemistry of sulfur–nitrogen oxides in aqueous solution can be summarized by the overall Scheme 1, which is based on literature information[3,27] and our own experience in this field.[1,2,10,13,15,28] It is known that the oxides investigated undergo acid-catalysed hydrolysis reactions, which restrict the present investigation to $pH \geqslant 3$.[10,29–34] As was found for manganese(III),[15] the presence of iron(III) species induces the hydrolysis reaction and no other products than those usually found during acid hydrolysis were detected by ion chromatography.

The IR measurements of the gas phase of the reaction between iron(III) perchlorate and $HONH(SO_3)^-$ clearly showed the formation of $N_2O$. Thus redox chemistry occurs, since $N_2O$ is the oxidation product of this ion.

### Reduction of $Fe^{III}$

Iron(III) in an azide medium is characterized by two absorbance maxima at 340 and 470 nm, whereas in perchlorate, chloride, sulfate and acetate media no characteristic absorbance maximum is present. Iron(III) is characterized by an absorbance maximum at 280 nm in the presence of a large excess of formate. Upon addition of $HONH(SO_3)^-$ or $HON(SO_3)_2^{2-}$ to a solution containing iron(III) in one of these media a decrease in the iron(III) concentration is observed as shown for the case of iron(III) perchlorate in Fig. 2. In most cases the reactions consist of two steps, a fast and a slow one, in contrast to one step usually observed in the case of manganese(III).[15] In general the OLIS KINFIT program was adopted to fit the two exponential functions. In some cases the rate constants were too similar and a single exponential gave a better fit of the data (see subsequent tables). In comparison to the reactivity of manganese(III), iron(III) also reacts faster with $HONH(SO_3)^-$ than it does with $HON(SO_3)_2^{2-}$. In the case of fast overall reactions the $k_{obs}$ values vary linearly with the concentration of the oxide for both reaction steps [most reactions of the iron(III) species with $HONH(SO_3)^-$ can be measured on a stopped-flow spectrophotometer]. Such a dependence was found for the reaction of $HONH(SO_3)^-$ with iron(III) in perchlorate, chloride, sulfate and formate media, and for the slow reaction step of $HON(SO_3)_2^{2-}$ with iron(III) in chloride medium (Table 1). In the latter case the fast reaction step exhibits a significant intercept (see further discussion).

The linear concentration dependence of $k_{obs}$ on [oxide] as expressed in equation (4) indicates that these sulfur–nitrogen

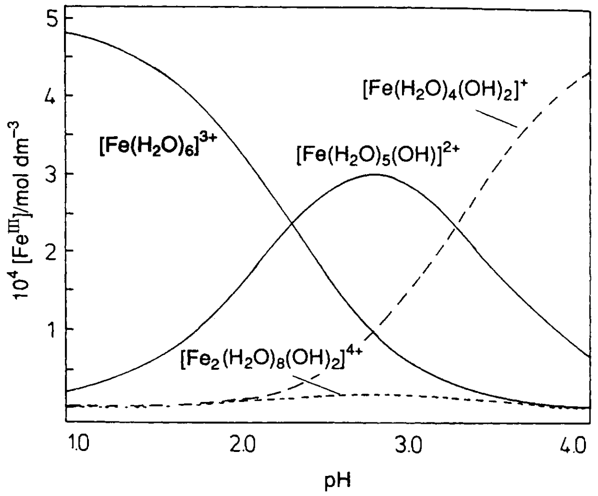


**Fig. 1** Distribution curves for the various iron species in aqueous acidic solution as a function of pH;[26] $[Fe^{III}] = 5 \times 10^{-4}$ mol $dm^{-3}$, $I \approx 0$ mol $dm^{-3}$, $T = 25$ °C

$$k_{obs} = k_1[\text{oxide}] \qquad (4)$$

oxides are involved in the rate-determining step of the reaction, but no distinction between an inner- or outer-sphere electron-transfer mechanism can be made on the basis of this relationship. The high lability of the iron pentaaquahydroxo complex would, however, favour the operation of an inner-sphere mechanism. In the case of the two steps observed for the reaction between iron(III) perchlorate and $HONH(SO_3)^-$ the fast reaction presumably corresponds to the reduction of the labile iron(III) pentaaquahydroxo complex by this ion, whereas the slow reaction represents the reduction of higher-order iron hydroxo species (di- or poly-meric). The high reactivity of the iron(III) pentaaquahydroxo species has also been found in another investigation.[35] Both reactions depend on the concentration of $HONH(SO_3)^-$. The iron(III) species rapidly co-ordinates this ion in a first step [equation (5)]. The

$$Fe^{III}L + HONH(SO_3)^- \rightleftharpoons [Fe^{III}L\{HONH(SO_3)\}]^- \qquad (5)$$

intermediate formed reacts subsequently to give the final products [equations (6)–(8); L = $H_2O$, $OH^-$, $X^-$ (anions, *e.g.* $Cl^-$, $SO_4^{2-}$, *etc.*)].

$$[Fe^{III}L\{HONH(SO_3)\}]^- + H_2O \longrightarrow Fe^{II}L + NHOH + H^+ + HSO_4^- \qquad (6)$$

$$2\,NHOH \longrightarrow NH_2OH + HNO \qquad (7)$$

$$2\,HNO \longrightarrow N_2O + H_2O \qquad (8)$$

In the suggested mechanism reaction (5) can be a rapid pre-equilibrium ($K_3$) followed by the rate-determining electron-transfer step (6). In such a case $k_{obs} = k_4K_3[\text{oxide}]$ under the experimental conditions in the present study, *viz.* $k_{obs}$ depends linearly on the [oxide] as expressed by equation (4). In the presence of anionic ligands reaction (5) can be significantly slower and represent the substitution-controlled process. Under these conditions the rate equation could be of the form $k_{obs} = k_{-3} + k_3[\text{oxide}]$ (see below). During the reduction of iron(III) to iron(II) by $HONH(SO_3)^-$ both the hydrolysis products of the ion ($NH_2OH$ and sulfate) and $N_2O$ as oxidation product are formed. The gas $N_2O$ can be detected by IR measurements, the characteristic bands being at 2210 and 2234 $cm^{-1}$. A decrease in velocity accompanies a reduction in pH from 3 to 2; this is due to the different distribution of the various iron species (Fig. 1).[26] At pH 2 the amount of the reactive iron(III) pentaaquahydroxo species and of the higher iron(III) hydroxo species is lower than at pH 3; therefore, the reaction is slower at lower pH. This indicates that the substitution reaction (5) plays an important role in the overall electron-transfer process. When the pH is increased to 4 the absorbance changes become smaller and therefore no exact kinetic measurements could be made.

A change of the iron medium from perchlorate to chloride, sulfate or formate resulted in a decrease in the rate constant values for both reaction steps, as shown in Table 2. According to the available stability-constant data,[36,37] chloride, sulfate and formate are stronger complexing reagents than perchlorate, and in turn sulfate forms stronger iron(III) complexes than chloride and formate stronger ones than chloride or sulfate. Obviously, the stronger complexing agents diminish the amount of the reactive iron(III) hydroxo species by forming complexes in which one or more anions are co-ordinated. This shows that ligand substitution plays an important role and controls the overall redox reaction. In the case of acetate and azide, complex formation is so effective[38,39] that the reduction of iron(III) in these media is very slow (Table 3). Furthermore, in the pH range of these media (5–6) almost no reactive iron species exist. The slow reduction of iron(III) azide and iron(III) acetate by $HONH(SO_3)^-$ is presumably independent of the oxide concentration (Table 3). This means that the electron-transfer reaction (6) itself must be the rate-determining step; it must be an intramolecular process within the precursor complex rapidly produced in (5). The reaction of iron(III) azide with $HONH(SO_3)^-$, in contrast to the other reactions, exhibits a single reaction step. Only at very high excess of oxide $\{[Fe^{III}] = 1 \times 10^{-4}$; $[HONH(SO_3)^-] > 6 \times 10^{-3}$ mol dm$^{-3}\}$ could two reaction steps be observed. Furthermore, iron(III) azide is able to perform a redox cycle with $HONH(SO_3)^-$ (Fig. 3), due to the oxygen sensitivity of the reduced iron(II) azide product. In the absence of oxygen, $HONH(SO_3)^-$ reduces the iron(III) azide to iron(II) azide. The absorbance of the two characteristic maxima of iron(III) azide at 340 and 470 nm decreases as a function of time (Fig. 3). When oxygen is added to induce the back reaction the reoxidation of the oxygen-sensitive iron(II) azide to iron(III) azide takes place accompanied by a build-up of the two absorbance maxima of iron(III) azide (Fig. 3).

The interaction of $HON(SO_3)_2^{2-}$ with iron(III) exhibits, in

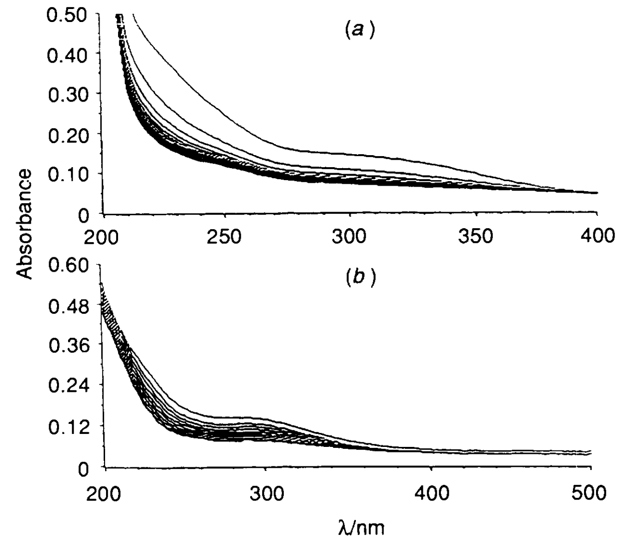


**Fig. 2** Reduction of iron(III) perchlorate. Experimental conditions: $[Fe^{III}] = 1 \times 10^{-4}$ mol dm$^{-3}$; pH 3; $T$ = 25 °C; $I$ = 0.1 mol dm$^{-3}$: (*a*) $[HONH(SO_3)^-] = 1 \times 10^{-3}$ mol dm$^{-3}$; $\Delta t$ = 10 s; (*b*) $[HON(SO_3)_2^{2-}] = 1 \times 10^{-3}$ mol dm$^{-3}$, $\Delta t$ = 500 s

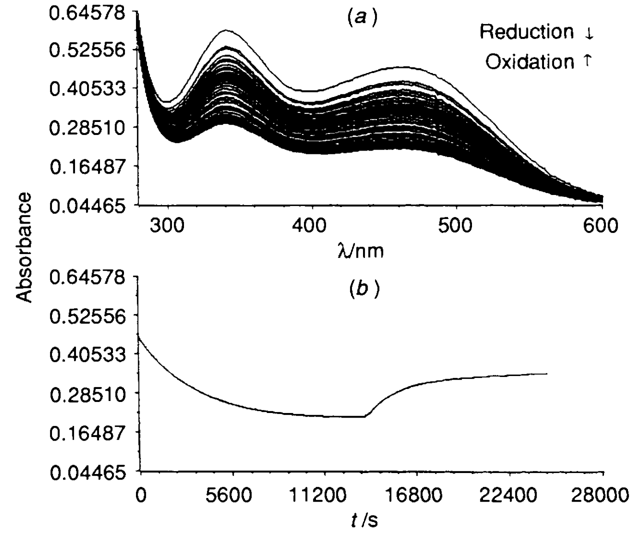


**Fig. 3** Reduction and oxidation of iron(III) azide in the presence of $HONH(SO_3)^-$; (*a*) UV/VIS spectra, $[Fe^{III}] = 1 \times 10^{-4}$ mol dm$^{-3}$; $[HONH(SO_3)^-] = 1 \times 10^{-3}$ mol dm$^{-3}$; $[N_3^-] = 0.3$ mol dm$^{-3}$; pH 5.5; $T$ = 25 °C, $\Delta t$ = 20 s; (*b*) absorbance *vs.* time trace of the same reaction at 480 nm

**Table 1** Summary of $k_{obs}$ values for the reduction of iron(III) in different media as a function of the oxide concentration. $I$ = 0.1 mol dm$^{-3}$, 25 °C

| Medium | Oxide | $10^3$Oxide/mol dm$^{-3}$ | Step | $k_{obs}$/s$^{-1}$ | pH |
|---|---|---|---|---|---|
| 0.1 ml dm$^{-3}$ $NaClO_4$ | $HONH(SO_3)^-$ | 1 | 1 | 2.16 ± 0.6 | 3 |
| | | | 2 | 0.398 ± 0.04 | |
| | | 2 | 1 | 3.01 ± 0.5 | |
| | | | 2 | 0.50 ± 0.09 | |
| | | 4 | 1 | 6.48 ± 0.3 | |
| | | | 2 | 0.99 ± 0.04 | |
| | | 6 | 1 | 9.18 ± 0.8 | |
| | | | 2 | 1.41 ± 0.26 | |
| 0.1 mol dm$^{-3}$ NaCl | $HONH(SO_3)^-$ | 1 | 1 | 0.67 ± 0.16 | 3 |
| | | | 2 | 0.11 ± 0.02 | |
| | | 2 | 1 | 1.87 ± 0.13 | |
| | | | 2 | 0.25 ± 0.01 | |
| | | 4 | 1 | 3.29 ± 0.23 | |
| | | | 2 | 0.45 ± 0.02 | |
| | | 6 | 1 | 5.05 ± 0.8 | |
| | | | 2 | 0.79 ± 0.15 | |
| | $HON(SO_3)_2^{2-}$ | 1 | 1 | 0.011 ± 0.001 | 3 |
| | | | 2 | (2.1 ± 0.2) × $10^{-4}$ | |
| | | 2 | 1 | 0.011 ± 0.001 | |
| | | | 2 | (5.1 ± 0.2) × $10^{-4}$ | |
| | | 4 | 1 | 0.016 ± 0.001 | |
| | | | 2 | (7.7 ± 2.1) × $10^{-4}$ | |
| | | 6 | 1 | 0.02 ± 0.001 | |
| | | | 2 | (9.5 ± 0.1) × $10^{-4}$ | |
| 0.1 mol dm$^{-3}$ $Na_2SO_4$* | $HONH(SO_3)^-$ | 1 | 1 | 0.06 ± 0.003 | 3 |
| | | | 2 | (8.5 ± 0.3) × $10^{-3}$ | |
| | | 2 | 1 | 0.13 ± 0.01 | |
| | | | 2 | (21 ± 0.7) × $10^{-3}$ | |
| | | 4 | 1 | 0.31 ± 0.03 | |
| | | | 2 | 0.050 ± 0.001 | |
| | | 6 | 1 | 0.48 ± 0.06 | |
| | | | 2 | 0.082 ± 0.002 | |
| 0.1 mol dm$^{-3}$ $Na(O_2CH)$ | $HONH(SO_3)^-$ | 1 | 1 | (2.3 ± 0.2) × $10^{-2}$ | 3.6 |
| | | | 2 | (4.7 ± 0.3) × $10^{-3}$ | |
| | | 2 | 1 | (3.1 ± 0.1) × $10^{-2}$ | |
| | | | 2 | (7.3 ± 0.1) × $10^{-3}$ | |
| | | 4 | 1 | (7.4 ± 0.95) × $10^{-2}$ | |
| | | | 2 | (1.7 ± 0.1) × $10^{-2}$ | |

* $I$ = 0.3 mol dm$^{-3}$.

**Table 2** Values of $k$ for the reduction of the different iron(III) species by $HONH(SO_3)^-$ 25 °C; $I$ = 0.1 mol dm$^{-3}$

| Iron(III) complex | Reaction step | $k$/dm$^3$ mol$^{-1}$ s$^{-1}$ | pH |
|---|---|---|---|
| Perchlorate | 1 | 1456 ± 88 | 3 |
| | 2 | 210 ± 14 | |
| Chloride | 1 | 848 ± 48 | 3 |
| | 2 | 132 ± 11 | |
| Sulfate* | 1 | 85.6 ± 2 | 3 |
| | 2 | 14.7 ± 0.4 | |
| Formate | 1 | 17.6 ± 3.5 | 3.6 |
| | 2 | 4.1 ± 0.5 | |

* $I$ = 0.3 mol dm$^{-3}$.

**Table 3** Summary of kinetic data for the reduction of iron(III) (1 × $10^{-4}$ mol dm$^{-3}$) by $HONH(SO_3)^-$ at 25 °C (*a*) in acetate medium: $[CH_3CO_2^-]$ = 0.1 mol dm$^{-3}$; pH = 6; λ = 250 nm; (*b*) in azide medium: $[Fe^{III}]$ = 1 × $10^{-4}$ mol dm$^{-3}$; $[N_3^-]$ = 0.3 mol dm$^{-3}$; pH = 5.5; λ = 340 nm

| $10^3[HONH(SO_3)^-]$/mol dm$^{-3}$ | Reaction step | $k_{obs}{}^a$/s$^{-1}$ |
|---|---|---|
| (*a*)[a] | | |
| 1 | 1 | (1.5 ± 0.2) × $10^{-3}$ |
| | 2 | (3.9 ± 0.8) × $10^{-5}$ |
| 2 | 1 | (1.5 ± 0.4) × $10^{-3}$ |
| | 2 | (7.6 ± 0.5) × $10^{-5}$ |
| 4 | 1 | (1.5 ± 0.2) × $10^{-3}$ |
| | 2 | (1.1 ± 0.1) × $10^{-4}$ |
| 6 | 1 | (9.5 ± 0.7) × $10^{-4}$ |
| | 2 | (2.0 ± 0.5) × $10^{-5}$ |
| 8 | 1 | (1.3 ± 0.1) × $10^{-3}$ |
| | 2 | (9.5 ± 0.5) × $10^{-5}$ |
| 10 | 1 | (1.4 ± 0.1) × $10^{-3}$ |
| | 2 | (5.6 ± 0.3) × $10^{-5}$ |
| (*b*)[b] | | |
| 1 | 1 | (3.2 ± 0.1) × $10^{-4}$ |
| 2 | 1 | (6.3 ± 0.2) × $10^{-4}$ |
| 4 | 1 | (7.0 ± 0.2) × $10^{-4}$ |
| 6 | 1 | (6.6 ± 0.3) × $10^{-4}$ |
| 8 | 1 | (7.5 ± 0.1) × $10^{-4}$ |
| | 2 | (1.3 ± 0.2) × $10^{-4}$ |
| 10 | 1 | (1.8 ± 0.1) × $10^{-3}$ |
| | 2 | (7.0 ± 0.3) × $10^{-4}$ |

[a] Average values of $k_{obs}$: first reaction step, (1.4 ± 0.2) × $10^{-3}$; second reaction step, (6 ± 3) × $10^{-5}$ s$^{-1}$. [b] Average value of $k_{obs}$: (6 ± 2) × $10^{-4}$ s$^{-1}$.

the case of perchlorate and sulfate, two reaction steps without a clear dependence of $k_{obs}$ on the oxide concentration, which indicates that the electron-transfer reaction (6) is the rate-determining step (Tables 4 and 5). The fast reaction is the reduction of the labile monohydroxo species, whereas the slow reaction is a measure of the reduction of a higher-order iron hydroxo species in the case of the perchlorate medium. In sulfate-containing media the slower reaction can be attributed to a reduction due to an iron(III) sulfato species. In general, rate data for the second reaction step are subject to large error limits such that these should not be overinterpreted.

A concentration dependence of $k_{obs}$ on the [oxide] was observed for the reduction of iron(III) chloride by $HON(SO_3)_2^{2-}$ (Table 1). A plot of $k_{obs}$ *versus* $[HON(SO_3)_2^{2-}]$ (Fig. 4) clearly shows that the fast reaction exhibits a significant

**Table 4** Summary of kinetic data for the reduction of iron(III) perchlorate by $HON(SO_3)_2^{2-}$. Experimental conditions: $[Fe^{III}] = 5 \times 10^{-4}$ mol dm$^{-3}$, $I = 0.1$ mol dm$^{-3}$, pH 3, 25 °C, $\lambda = 365$ nm

| $10^3[HON(SO_3)_2^{2-}]$/mol dm$^{-3}$ | Reaction step | $k_{obs}$*/s$^{-1}$ |
|---|---|---|
| 5 | 1 | $(1.30 \pm 0.06) \times 10^{-3}$ |
| | 2 | $(1.29 \pm 0.01) \times 10^{-4}$ |
| 6 | 1 | $(1.0 \pm 0.01) \times 10^{-3}$ |
| | 2 | $(1.72 \pm 0.02) \times 10^{-4}$ |
| 8 | 1 | $(1.13 \pm 0.02) \times 10^{-3}$ |
| | 2 | $(1.6 \pm 0.1) \times 10^{-4}$ |
| 10 | 1 | $(1.01 \pm 0.02) \times 10^{-3}$ |
| | 2 | $(1.85 \pm 0.03) \times 10^{-4}$ |
| 15 | 1 | $(1.18 \pm 0.07) \times 10^{-3}$ |
| | 2 | $(2.76 \pm 0.02) \times 10^{-4}$ |

* Average values of $k_{obs}$: first reaction step, $(1.1 \pm 0.1) \times 10^{-3}$, second reaction step, $(1.8 \pm 0.5) \times 10^{-4}$ s$^{-1}$.

**Table 5** Summary of kinetic data for the reduction of iron(III) sulfate by $HON(SO_3)_2^{2-}$. Experimental conditions: $[Fe^{III}] = 1 \times 10^{-4}$ mol dm$^{-3}$, pH 3. $I = 0.3$ mol dm$^{-3}$ ($Na_2SO_4$), 25 °C, $\lambda = 300$ nm

| $10^3[HON(SO_3)_2^{2-}]$/mol dm$^{-3}$ | Reaction step | $k_{obs}$*/s$^{-1}$ |
|---|---|---|
| 1 | 1 | $(5.6 \pm 0.1) \times 10^{-3}$ |
| | 2 | $(8.0 \pm 0.1) \times 10^{-4}$ |
| 2 | 1 | $(6.7 \pm 0.2) \times 10^{-3}$ |
| | 2 | $(7.8 \pm 0.1) \times 10^{-4}$ |
| 4 | 1 | $(5.8 \pm 1.5) \times 10^{-3}$ |
| | 2 | $(6.4 \pm 3.8) \times 10^{-4}$ |
| 6 | 1 | $(5.5 \pm 0.3) \times 10^{-3}$ |
| | 2 | $(2.9 \pm 0.8) \times 10^{-4}$ |

* Average values of $k_{obs}$: first reaction step, $(5.9 \pm 0.5) \times 10^{-3}$; second reaction step, $(6 \pm 2) \times 10^{-4}$ s$^{-1}$.

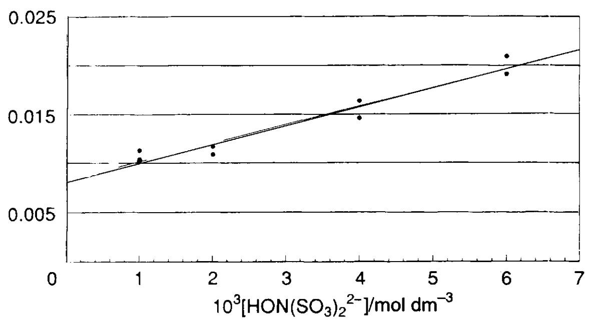


**Fig. 4** Plot of first-order rate constant *versus* $[HON(SO_3)_2^{2-}]$ for the fast reaction step of the reduction of iron(III) chloride by $HON(SO_3)_2^{2-}$

**Table 6** Comparison of kinetic data for the reduction of (*a*) iron(III) and (*b*) manganese(III) in azide medium at pH 5.5 and 25 °C. Experimental conditions: (*a*) $[Fe^{III}] = 1 \times 10^{-4}$ mol dm$^{-3}$, $[N_3^-]_T = 0.3$ mol dm$^{-3}$; $\lambda = 340$ nm; (*b*) $[Mn^{III}] \times 4 \times 10^{-5}$ mol dm$^{-3}$, $[Mn^{II}] = 0.1$ mol dm$^{-3}$, $[N_3^-]_T = 0.25$ mol dm$^{-3}$; $420 < \lambda < 500$ nm[15]

| | $k_{obs}$/s$^{-1}$ | |
|---|---|---|
| $10^3[HONH(SO_3)^-]$/ mol dm$^{-3}$ | $Fe^{III}$ | $Mn^{III}$ |
| 2 | $(6.3 \pm 0.2) \times 10^{-4}$ | $5.8 \pm 0.2$ |
| 4 | $(7.0 \pm 0.2) \times 10^{-4}$ | $11.6 \pm 0.4$ |
| 6 | $(6.6 \pm 0.3) \times 10^{-4}$ | $17.4 \pm 0.6$ |

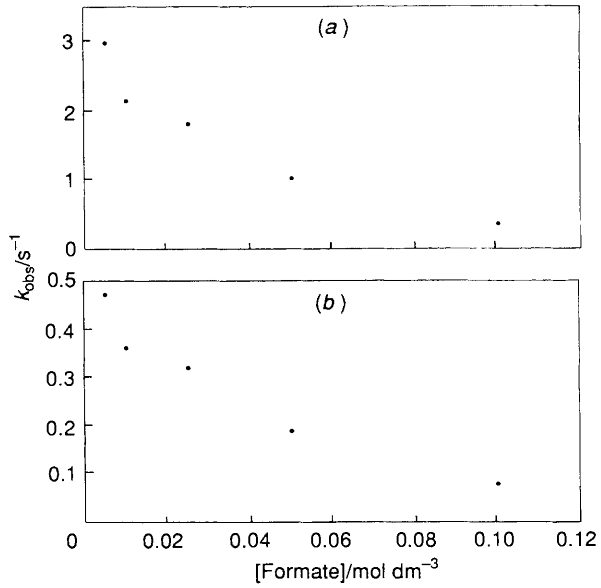


**Fig. 5** Formate dependence for the two reaction steps [fast (*a*), slow (*b*)] in the reduction of iron(III) formate with $HONH(SO_3)^-$. Experimental conditions: $[Fe^{III}] = 1 \times 10^{-4}$ mol dm$^{-3}$, $[HONH(SO_3)^-] = 3 \times 10^{-3}$ mol dm$^{-3}$, pH 3.6, $T = 25$ °C, $\lambda = 320$ nm, $I = 0.1$ mol dm$^{-3}$

intercept. In contrast, the slow reaction (data in Table 1) exhibits almost a linear concentration dependence with no significant intercept. The intercept for the fast reaction can either be due to the reverse reaction (5) (see above) or indicate that a parallel reaction path may be involved, independent of the concentration of $HON(SO_3)_2^{2-}$. This path could for instance represent the rate-determining dissociation of dimeric species to produce the more reactive monomeric species. This would again suggest that the fast reaction is substitution controlled. Alternatively, rapid formation of the inner-sphere species in (5) followed by rate-determining intramolecular electron-transfer (intercept) could be paralleled by an outer-sphere reaction path that will depend on the $[HON(SO_3)_2^{2-}]$ (slope). The $k$ values ($k_1 = 1.9 \pm 0.2$, $k_2 = 0.15 \pm 0.02$ dm$^3$ mol$^{-1}$ s$^{-1}$) of this reaction are much smaller than the values of the analogous reaction with $HONH(SO_3)^-$ ($k_1 = 848 \pm 48$; $k_2 = 132 \pm 11$ dm$^3$ mol$^{-1}$ s$^{-1}$) since $HONH(SO_3)^-$ is a stronger nucleophile and/or a better reducing agent than $HON(SO_3)_2^{2-}$. The latter is not able effectively to reduce the strong iron(III) formate, acetate and azide complexes under the selected conditions ($I = 0.1$ mol dm$^{-3}$). The ions $N(SO_3)_3^{3-}$ and $HN(SO_3)_2^{2-}$ were found not to react with the labile monohydroxo species of $Fe^{III}$.

## Comparison between iron and manganese

A comparison of the kinetic data for the reaction of iron(III) and manganese(III) in azide and acetate medium by $HONH(SO_3)^-$ (Tables 6 and 7) indicates that manganese(III) is much more reactive than iron(III). The much faster reactions of manganese(III) show a linear dependence of $k_{obs}$ on the concentration of $HONH(SO_3)^-$ in contrast to the slow reactions of iron(III), where no concentration dependence of the rate constant was found. In the case of the slow reacting iron(III) azide and acetate systems the electron-transfer reaction seems to be the rate-determining step.

In most of the reactions studied an increase in the concentration of the anions (chloride, sulfate, formate, acetate, *etc.*) causes inhibition to a varying extent depending on the nature of the anions. The extent is directly related to the complexing ability of the anions. An increase in the formate concentration (Fig. 5) results in a significant decrease in the velocity of the reduction of iron(III) formate by $HONH(SO_3)^-$ in both reaction steps. In addition, the reduction in this case also depends on pH because this controls the concentration of formate ions in solution. It is therefore difficult to obtain satisfactorily reproducible kinetic data near the p$K_a$ value of formic acid since a small change in pH is associated with a large change in the distribution between formic acid and formate ions.

**Table 7** Comparison of the kinetic data for the reduction of (*a*) iron(III) and (*b*) manganese(III) in acetate medium at 25 °C. Experimental conditions (*a*) $[\mathrm{Fe^{III}}] = 1 \times 10^{-4}$ mol dm$^{-3}$, $[\mathrm{MeCO_2^-}]_T = 0.1$ mol dm$^{-3}$, pH 6, $\lambda = 250$ nm; (*b*) $[\mathrm{Mn^{III}}] = 5 \times 10^{-5}$ mol dm$^{-3}$; $[\mathrm{Mn^{II}}] = 0.5$ mol dm$^{-3}$, $[\mathrm{MeCO_2^-}]_T = 0.2$ mol dm$^{-3}$; $I = 0.6$ mol dm$^{-3}$; pH 3, $\lambda = 500$ nm[15]

| | | $k_{obs}/s^{-1}$ | |
|---|---|---|---|
| $10^3[\mathrm{HONH(SO_3)^-}]$/mol dm$^{-3}$ | Reaction step | $\mathrm{Fe^{III}}$ | $\mathrm{Mn^{III}}$ |
| 1 | 1 | $(1.5 \pm 0.2) \times 10^{-3}$ | $0.59 \pm 0.01$ |
| | 2 | $(3.9 \pm 0.8) \times 10^{-5}$ | |
| 2 | 1 | $(1.5 \pm 0.4) \times 10^{-3}$ | $1.05 \pm 0.03$ |
| | 2 | $(7.6 \pm 0.5) \times 10^{-5}$ | |
| 4 | 1 | $(1.5 \pm 0.2) \times 10^{-3}$ | $1.89 \pm 0.04$ |
| | 2 | $(1.1 \pm 0.1) \times 10^{-4}$ | |

The iron(III)-catalysed hydrolysis reaction of the oxides probably follows an analogous pathway to that of the spontaneous and manganese(III)-catalysed hydrolysis reactions.[15] During the reaction involving $\mathrm{Fe^{III}}$ the nitrogen atom of the oxide co-ordinates to the metal, through which the hydrolysis process is induced. In the case of the hydrolysis of $\mathrm{HON(SO_3)_2^{2-}}$ by $\mathrm{Fe^{III}}$, $\mathrm{HON(SO_3)^-}$ is formed as an intermediate, which then reacts further to form $\mathrm{HONH(SO_3)^-}$ and $\mathrm{N_2O}$ [equations (9)–(11) and (8); L = $\mathrm{H_2O}$, $\mathrm{OH^-}$, $\mathrm{X^-}$ (anions, *e.g.* $\mathrm{Cl^-}$, $\mathrm{SO_4^{2-}}$, *etc.*)].

$$\mathrm{Fe^{III}L + HON(SO_3)_2^{2-} \rightleftharpoons [Fe^{III}L\{HON(SO_3)_2\}]^{2-}} \quad (9)$$

$$\mathrm{[Fe^{III}L\{HON(SO_3)_2\}]^{2-} + H_2O \longrightarrow Fe^{II}L + HON(SO_3)^- + H^+ + HSO_4^-} \quad (10)$$

$$\mathrm{2\,HON(SO_3)^- + H_2O \longrightarrow HONH(SO_3)^- + HNO + HSO_4^-} \quad (11)$$

$$\mathrm{2\,HNO \longrightarrow N_2O + H_2O} \quad (8)$$

The rate of co-ordination of the iron with the oxide depends on the nature and the concentration of the anion, on the pH of the solution and on the reducing strength of the oxide. The stronger the complexing ability of the anions, the slower the oxide co-ordinates, since the concentration of the reactive iron monohydroxo species is reduced under such conditions. This is a consequence of the formation of less-reactive complexes of iron with the anions. The higher the anion concentration the more of these complexes (1 : 1, 1 : 2, *etc.*) are formed. In addition, an increase in pH has a similar effect due to the formation of less-reactive iron hydroxo species (*viz.* dimers and polymers). The velocity of the reduction reaction depends on the reducing ability of the oxide: $\mathrm{HONH(SO_3)^-}$ is a stronger reducing agent than $\mathrm{HON(SO_3)_2^{2-}}$.

The possibility of a synergistic effect between manganese(II) and iron(III) was also investigated. It is known[40–42] that there is a strong synergistic effect of these ions in the autoxidation reaction of sulfur(IV). The reduction of manganese(III) by $\mathrm{HONH(SO_3)^-}$ was investigated in the presence and absence of iron(III) in azide media, but no synergistic effect was observed. This indicates that in this case the produced iron species [iron(III) azide] is too inert to participate in a synergistic reaction sequence.

## Conclusion

The results reported demonstrate that the sulfur–nitrogen oxides studied are able to reduce iron(III) ions and complexes within a wide pH range. Therefore the concentration of the catalytic species available for the autoxidation of sulfur(IV) oxides is diminished, which leads to an inhibition of the autoxidation process. In comparison with manganese(III), the effect of iron(III) is significantly smaller (factor $10^3$–$10^4$) due to the fact that manganese(III) is a stronger oxidizing agent than iron(III).

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