Reaction of Nitric Oxide with Sulfur(IV) Oxides in the Presence of Iron(II) Complexes in Aqueous Solution

Volker Zang and Rudi van Eldik *
Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, Federal Republic of Germany

Complexes of the type $Fe^{II}L$ (L = diethylenetriaminepentaacetate, ethylenediaminetetraacetate, *N*-2-hydroxyethylethylenediaminetriacetate or nitrilotriacetate) can effectively bind NO in aqueous solution to produce FeL(NO) species which can react with sulfur(IV) oxides to produce $Fe^{III}L$, N_2O, SO_4^{2-} and various nitrogen-sulfur oxides. The kinetics of these reactions was studied as a function of $[S^{IV}]_T$ and pH using stopped-flow and UV/VIS spectroscopic techniques. Depending on the selected experimental conditions, two subsequent reactions were observed: the first involved the reaction of unco-ordinated NO with sulfur(IV) oxides to produce mainly $^-ON(NO)SO_3^-$ whereas the second involved attack of sulfoxides on the co-ordinated NO (presumably as nitrosyl) according to the Boedeker process to produce $Fe^{III}L$, N_2O, SO_4^{2-} and $HON(SO_3)_2^{2-}$. Reactions were also studied in a flow reactor in which a stream of NO gas was passed through a $Fe^{II}L$–sulfite solution, and the reaction products were monitored on-line. The information obtained from both methods was used to suggest possible reaction mechanisms for the various steps. The results are discussed in reference to available literature information, and an overall catalytic cycle to account for the role of $Fe^{II}L$ is suggested.

We have in recent years developed an interest in the effect of metal ions and complexes on the oxidation processes of nitrogen and sulfur oxides in aqueous solution, and the possible role of such reactions in atmospheric oxidation processes, *i.e.* acid-rain formation. In this respect we have performed a series of studies on the reactions of iron(III) ions and complexes with sulfur(IV) oxides [1–5] and on the reactions of different iron(II) complexes with nitrogen oxides.[6,7] We have now combined these oxides and studied their reactions in the presence of a series of polyaminocarboxylate complexes of iron(II).[8]

It is generally known that nitrogen and sulfur oxides undergo a series of complex chemical reactions in aqueous solution which result in the formation of various redox products and a series of N–S compounds.[9–14] It is especially the redox behaviour of nitric oxide with sulfite that has received substantial attention in recent years since this reaction could play an important role in the industrial cleaning of gaseous effluents from power plants through the suggested simultaneous absorption of NO and SO_2. In such processes iron(II) and other transition-metal complexes are added to improve the absorption of the weakly soluble NO and to bind it in the form of nitrosyl complexes.[15–22] These metal complexes form an integral part of the overall reaction mechanism and catalyse the reactions between the nitrogen and sulfur oxides. Various mechanistic aspects of these reactions are unresolved and will be treated in this report.

Our interest in these reactions also concerns their possible role in atmospheric oxidation processes, *i.e.* to what extent can the interaction of nitrogen and sulfur oxides be affected by metal ions and complexes. Most investigations have studied the possible role of metal ions and complexes in the oxidation reaction of sulfur(IV) oxides,[1–4,23–31] but little is known about the effect of nitrogen oxides. For this reason we selected a series of polyaminocarboxylate complexes of Fe^{II}, which are known to absorb NO effectively and create the possibility to vary systematically the number of blocked co-ordination sites as well as the lability of the co-ordinated solvent molecules.[32–35] These include the ligands diethylenetriaminepentaacetate (dtpa), ethylenediaminetetraacetate (edta), *N*-2-hydroxyethylethylenediaminetriacetate (hedtra) and nitrilotriacetate (nta). Two different approaches were adopted to investigate the reactions. In the first the kinetics of the reaction of complexes of the type $Fe^{II}L(NO)$ (L = polyaminocarboxylate ligand) with sulfite was studied as a function of different parameters. In the second, reaction mixtures containing $Fe^{II}L$ and sulfite were used to absorb nitric oxide in a flow reactor, and on-line analytical techniques were employed to monitor the composition of the reaction mixture in both the gas and aqueous phase. These approaches revealed complementary information on the overall process and contributed towards resolving some essential aspects of the underlying reaction mechanism.

Experimental

Chemicals of analytical reagent grade and deionized water were used to prepare all solutions. The employed gases NO and N_2 were 99 and 99.996% pure, respectively. The $Fe^{II}L$ complexes were prepared in solution from $FeSO_4$ and H_5dtpa, $Na_2(H_2edta)$, Na_3(hedtra) and H_3nta. Acetic acid–acetate and Tris buffer [Tris = tris(hydroxymethyl)methylamine] solutions were used to control the pH of the test solutions, whereas $NaClO_4$ was used to adjust the ionic strength. The $Fe^{II}L$ complexes are extremely oxygen sensitive, which required special handling[32] to prevent formation of $Fe^{III}L$. The $Fe^{II}L(NO)$ complexes were prepared from a large excess of $Fe^{II}L$ and NO.[6,7]

The UV/VIS spectra and slow kinetic traces were recorded in gas-tight, thermostatted (±0.1 °C) cuvettes in Shimadzu UV 250 and UV 2100 spectrophotometers. Faster reactions were followed on a modified Aminco stopped-flow instrument attached to an on-line data-acquisition system.[36] Gaseous products were analysed on a mass spectrometer and in the gas cell of a Nicolet 5 SX FT-IR instrument. The iron(II) concentration was monitored during the reaction of $Fe^{II}L(NO)$ with HSO_3^-/SO_3^{2-} using the standard phenanthroline method.

The flow reactor (see Fig. 1) consisted of a thermostatted double-walled glass reaction vessel (1.2 l) which contained various inlet and outlet connections. Two rotameters were employed to regulate the flow and composition of the NO–N_2 gas stream through the reaction vessel. Samples for chemical

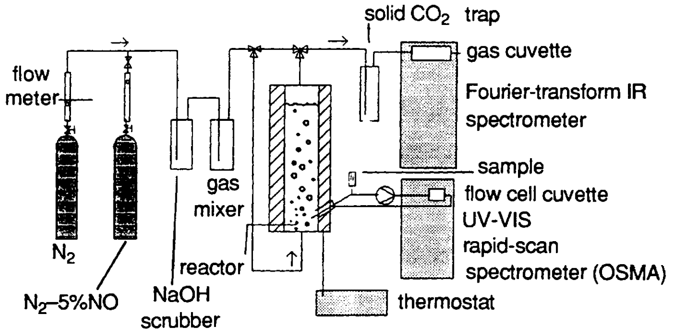


Fig. 1 Schematic representation of the flow reactor

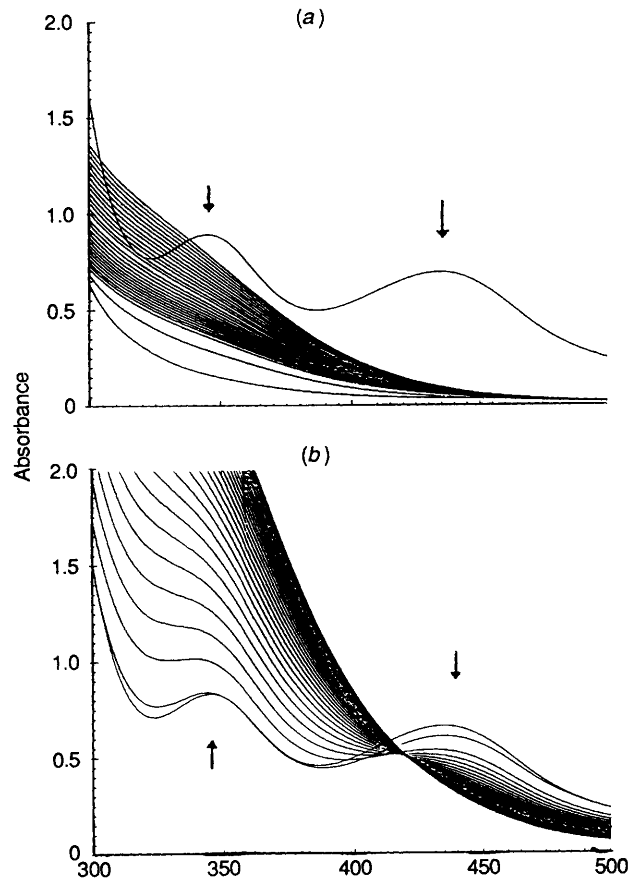


Fig. 2 Spectral changes observed during the reaction of Fe(dpta)(NO) with sulfite. Experimental conditions: [Fe(dtpa)] = 1.0×10^{-3} mol dm^{-3}, $[S^{IV}]_T$ = 2.0×10^{-2} mol dm^{-3}; Δt = 300 s; T = 25.0 °C; first spectrum recorded before addition of sulfite; pH 8.0 (*a*), 5.0 (*b*)

analysis could be withdrawn from the vessel *via* a septum. The UV/VIS spectra of the reaction mixture were monitored continuously using a circulation pump, a flow cuvette, and an OSMA rapid-scan spectrometer. The gas stream leaving the reactor was led through a cold trap, to remove water vapour, into a gas cuvette (pathlength 10 cm) and analysed continuously on the FT-IR instrument.

Results and Discussion

Kinetic Measurements.—The reactions of Fe^{II}L(NO) with HSO_3^-/SO_3^{2-} were studied at 25 °C and ionic strength 0.5 mol dm^{-3} under pseudo-first-order conditions, *i.e.* at least a ten-fold excess of sulfite. The complexes were characterized as described before.[6,7] The nature of the polyaminocarboxylate ligand determines the number of labile co-ordination sites on the Fe^{II}L centre. Addition of sulfite resulted in characteristic spectral changes depending on the pH of the solution. Two typical examples for L = dtpa and edta are illustrated in Figs 2 and 3, respectively. In general two subsequent reaction steps were observed for all investigated ligands,[8] which are accompanied by characteristic spectral changes. The first step is accompanied by a significant decrease in intensity of the absorption bands characteristic for Fe^{II}L(NO), followed in the second step by a significant absorbance increase at lower wavelength due to the formation of Fe^{III}L(SO_3). The iron(III) complex is only produced during the second step, and chemical analyses indicate a 1:1 ratio between the decrease in the [Fe^{II}] and increase in [Fe^{III}]. The examples in Figs. 2 and 3 demonstrate that the ability to separate the two reaction steps strongly depends on the pH of the solution. These spectral changes suggest that the [FeL(NO)] decreases in the first step due to the rapid consumption of NO, which is followed by a redox reaction and the production of Fe^{III}L(SO_3).

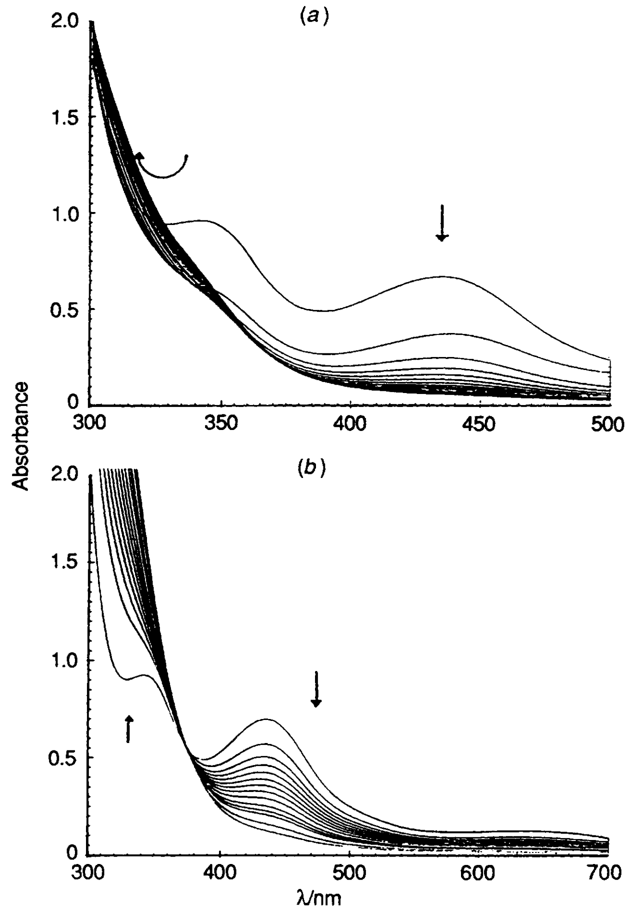


Fig. 3 Spectral changes observed during the reaction of Fe(edta)(NO) with sulfite. Experimental conditions: [Fe(edta)] = 1.0×10^{-3} mol dm^{-3}; $[S^{IV}]_T$ = 2.0×10^{-2} mol dm^{-3}; Δt = 120 (*a*), 180 s (*b*); T = 25.0 °C; first spectrum recorded before addition of sulfite; pH = 8.0 (*a*), 5.0 (*b*)

The first reaction can be followed especially well for the L = dtpa system. The results in Fig 4 demonstrate that the pseudo-first-order rate constant is proportional to the $[S^{IV}]_T$, and that it exhibits a characteristic pH dependence. Similar results were found for L = nta and over a limited pH range for L = edta since the first reaction does not show up at lower pH in this case.[8]

The spectroscopic and kinetic observations can be interpreted in terms of the mechanism outlined in Scheme 1 in which

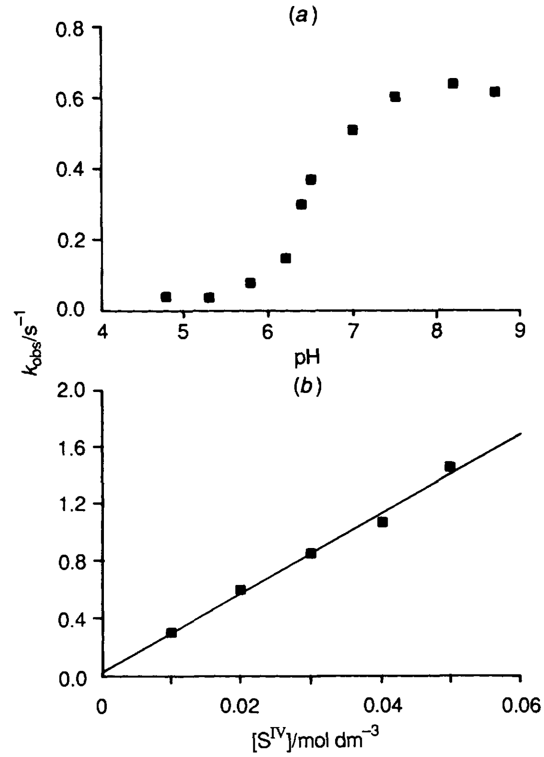


Fig. 4 The pH and $[S^{IV}]_T$ dependence of k_{obs} for the reactions in Scheme 1, L = dtpa. Experimental conditions: $[Fe^{II}L] = 1.0 \times 10^{-3}$ mol dm^{-3}; [buffer] = 0.05 mol dm^{-3}; T = 25.0 °C; I = 0.5 mol dm^{-3}; (*a*) $[S^{IV}]_T$ = 0.020 mol dm^{-3}, (*b*) pH 8.0

$$Fe^{II}L(NO) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{II}L + NO(aq)$$

$$NO(aq) + HSO_3^- \xrightarrow{k_2} ONSO_3^{2-} + H^+$$

$$NO(aq) + SO_3^{2-} \xrightarrow{k_3} ONSO_3^{2-}$$

$$ONSO_3^{2-} + NO(aq) \xrightarrow{fast} {}^-ON(NO)SO_3^-$$

Scheme 1

NO is released by $Fe^{II}L(NO)$ to react with HSO_3^-/SO_3^{2-} to produce $^-ON(NO)SO_3^-$. The reported pH dependence for L = dtpa and L = nta exhibits an inflection at pH ≈ 6.5, which is close to the pK_a value for HSO_3^-, *viz.* 6.3.[37] Furthermore, the data clearly indicate that $k_2 \ll k_3$, in agreement with literature[14] reports of these reactions in the absence of $Fe^{II}L$, *viz.* $k_2 = 32 \pm 10$ and $k_3 = 620 \pm 100$ dm^3 mol^{-1} s^{-1} at 25 °C. The observed rate constant for the disappearance of FeL(NO) can be expressed as in equation (1), where k'

$$k_{obs} = k_1k'[S^{IV}]/(k_{-1}[FeL] + k'[S^{IV}]) \quad (1)$$

represents k_2 or k_3 depending on the pH of the system. The data in Fig. 4 exhibit a linear dependence of k_{obs} on $[S^{IV}]_T$ such that equation (1) can be simplified to (2). Substitution of $k_1 = 23$ s^{-1}

$$k_{obs} = k_1k'[S^{IV}]/k_{-1}[FeL] \quad (2)$$

and $k_{-1} = 2.7 \times 10^5$ dm^3 mol^{-1} s^{-1} for L = dtpa[8] along with the cited values for k' ($= k_2$ or k_3) results in k_{obs} = 0.05 and 1.01 s^{-1} for $[S^{IV}]_T$ = 0.020 mol dm^{-3} at low and high pH, respectively. In these calculations it was assumed that [FeL] remains rather constant; only a small fraction is bound as FeL(NO) since a large excess of FeL was employed. The predicted values of k_{obs} are in rather close agreement with the limiting rate constants of 0.04 and 0.65 s^{-1}, respectively, reported in Fig. 4.

Similar relationships were observed for L = nta and edta. The observed rate constants in basic medium decrease in the sequence dtpa > nta > edta, which is in agreement with the trend in the formation constant K_1 ($= k_{-1}/k_1$), *viz.* 1.2×10^4, 2.1×10^6 and 1.1×10^7 dm^3 mol^{-1} for L = dtpa, nta and edta, respectively.[7,38] Thus only in the case of weakly co-ordinated NO, as for L = dtpa, will the reaction of unco-ordinated NO with S^{IV} dominate the process to produce $^-ON(NO)SO_3^-$, which can undergo acid hydrolysis to N_2O and SO_4^{2-} according to equation (3).[14] The formation of N_2O was

$$^-ON(NO)SO_3^- \xrightarrow{H^+} N_2O + SO_4^{2-} \quad (3)$$

demonstrated by sampling the gaseous reaction products with a gas cuvette and analysing the Fourier-transform IR spectra for bands at 2224 and 1285 cm^{-1},[39] and by recording the mass spectra (m/z = 44 for N_2O). No N_2O is produced when higher sulfite concentrations are employed owing to the dominant role of other reaction steps under such conditions (see further discussion). When NO is more tightly bound to the FeL centre as for the nta and edta complexes, then the reaction involving free NO becomes too slow to account for the observed data and an attack on the co-ordinated NO as indicated in equation (4) is

$$Fe^{II}L(NO) + HSO_3^-/SO_3^{2-} \longrightarrow Fe^{II}L + ONSO_3^{2-} \quad (4)$$

suggested. For this reaction another molecule of NO is required to produce $^-ON(NO)SO_3^-$, such that a high concentration of FeL(NO) or NO is needed.

The second slower reaction observed in Figs 2 and 3 is accompanied by the parallel oxidation of FeL and FeL(NO) to $Fe^{III}L$. The observed first-order rate constants depend linearly on $[S^{IV}]_T$, and some typical pH dependences are illustrated in Fig. 5. The rate constant k_{obs} increases with increasing pH in the range 4–7, reaches a maximum at pH > 7 for hedtra and nta, but decreases at pH > 7 for edta. The increase in k_{obs} with increasing pH is ascribed to the HSO_3^-/SO_3^{2-} equilibrium since it is known that the FeL(NO) complexes do not exhibit any characteristic changes in this pH range.[7,32] The decrease in reactivity observed for L = edta at pH > 7 can be due to some structural change on the Fe^{II}(edta)(NO) complex in terms of its co-ordination geometry that may also involve the co-ordination of OH^-, or is due to a direct interaction of base with the co-ordinated NO to produce a nitro complex that will exhibit a significantly lower reactivity with sulfite.[40,41] The characteristic acidity dependence observed at pH < 7 can be understood on the basis of the different redox potentials of −0.92 and +0.2 V for SO_3^{2-} and H_2SO_3, respectively,[42] since we are dealing with a redox process between S^{IV} and FeL(NO) in this reaction step. The rate constants follow the sequence edta > dtpa, nta ≫ hedtra in acidic media and edta, nta ≫ hedtra in basic media (the dtpa complex does not exhibit this reaction step in basic media).

On the basis of available literature information[17,18,22] it is safe to conclude that the reaction between nitrosyl complexes and sulfur(IV) oxides not only produces N_2O and SO_4^{2-}, but also a range of nitrogen–sulfur oxides of which hydroxylaminedisulfonate $HON(SO_3)_2^{2-}$ seems to be the major product. It is assumed that FeL(NO) reacts in a similar way as HONO or NO_2^- with HSO_3^-/SO_3^{2-} to form the disulfonate[11,12,43,44] which then can react with more sulfite to produce $NH(SO_3)_2^{2-}$[45] or in an acidic medium hydrolyse to hydroxylamine.[46] In basic medium $HON(SO_3)_2^{2-}$ can decompose *via* $HONH(SO_3)^-$ to N_2O and sulfite.[47] The formation of $HON(SO_3)_2^{2-}$ strongly depends on pH due to the hydrolysis of the $ONSO_3^-$ intermediate as indicated in Scheme 2.

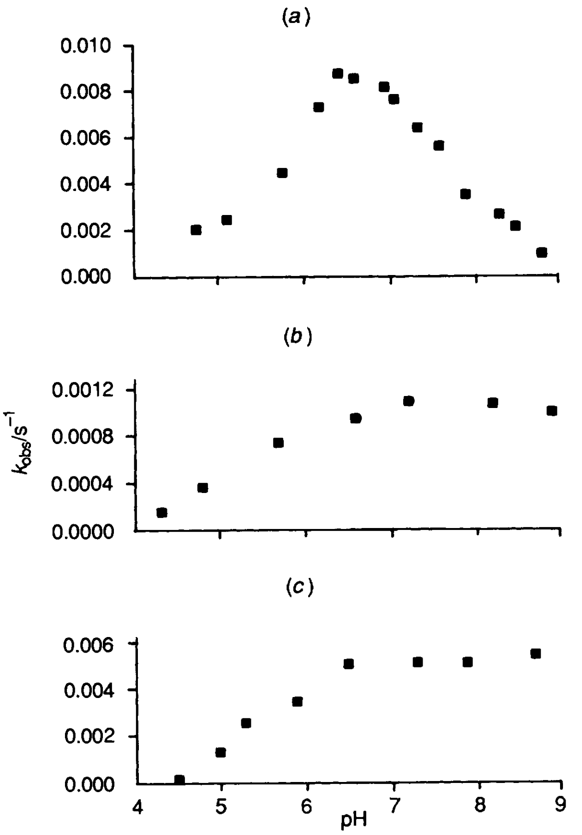
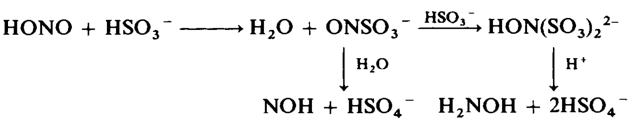


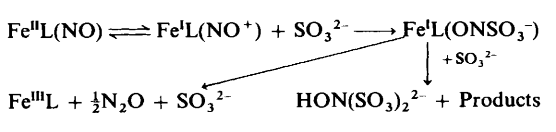
Fig. 5 Typical pH dependence of k_{obs} for the reactions in Scheme 3. Experimental conditions: $[Fe^{II}L] = 1.0 \times 10^{-3}$ mol dm^{-3}; $[S^{IV}]_T = 0.020$ mol dm^{-3}; [buffer] = 0.05 mol dm^{-3}; $T = 25.0$ °C; $I = 0.5$ mol dm^{-3}; L = edta (*a*), hedtra (*b*) or nta (*c*)



$$\begin{array}{ccc} HONO + HSO_3^- \longrightarrow & H_2O + ONSO_3^- \xrightarrow{HSO_3^-} & HON(SO_3)_2^{2-} \\ & \big\downarrow H_2O & \big\downarrow H^+ \\ & NOH + HSO_4^- & H_2NOH + 2HSO_4^- \end{array}$$

Scheme 2

On the basis of this information it is quite realistic to expect that $Fe^{II}L(NO)/S^{IV}$ can react in a similar way to produce $Fe^{III}L$ and $HON(SO_3)_2^{2-}$. This however requires that the co-ordinated NO must have nitrosyl character as indicated before.[7] This would account for the increased reactivity observed with increasing pH, since the reaction will then involve the more reactive SO_3^{2-} species. The overall reaction can be formulated as in Scheme 3, which is similar to the Boedeker reaction.[48]



$$\begin{array}{ccc} Fe^{II}L(NO) \rightleftharpoons Fe^{I}L(NO^+) + SO_3^{2-} \longrightarrow & & Fe^{I}L(ONSO_3^-) \\ & & \big\downarrow +SO_3^{2-} \\ Fe^{III}L + \tfrac{1}{2}N_2O + SO_3^{2-} & \longleftarrow & HON(SO_3)_2^{2-} + \text{Products} \end{array}$$

Scheme 3

The intermediate $Fe^{I}L(ONSO_3^-)$ species can react further in the same way as suggested in Scheme 2.

The product ratio will strongly depend on the selected reaction conditions and the nature of L. It was demonstrated[22] that the formation of $HON(SO_3)_2^{2-}$ is favoured by a high concentration of $Fe^{II}L$, whereas a high NO concentration resulted in a higher yield of N_2O. Under our selected conditions it can be assumed that mainly the reaction to N_2O and $Fe^{III}L$ will occur, in agreement with the 1:1 formation of $Fe^{III}L$ during the decomposition of $Fe^{II}L(NO)$ in the second reaction step observed in Figs. 2 and 3.

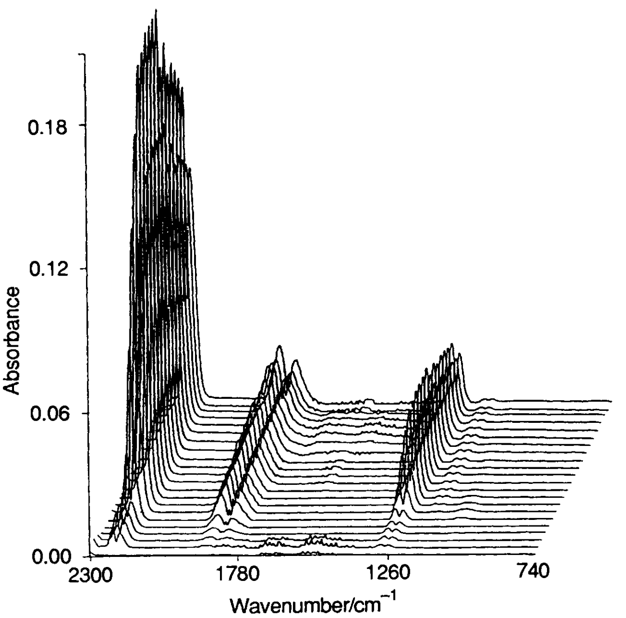


Fig. 6 Repetitive Fourier-transform IR spectra recorded for the gaseous effluents from the flow reactor for the Fe(hedtra)–NO–S^{IV} system at pH 8.0 (Δt = 5 min)

Flow-reactor Experiments.—The above reported kinetic data and mechanistic trends are nicely complemented by the results of flow-reactor experiments. For this purpose a stream of N_2 containing 0.57% NO was passed through a solution consisting of 2×10^{-3} mol dm^{-3} $Fe^{II}L$ and 4×10^{-2} mol dm^{-3} S^{IV} at a rate of 19.2 l h^{-1}. A 0.05 mol dm^{-3} buffer solution was employed to keep the pH at 5 (acetate buffer) or 8 (Tris buffer). Prior to the start of the experiment the solution was purged with N_2 for 20 min to remove all dissolved O_2 before the iron(II) salt was dissolved, to prevent oxidation to $Fe^{III}L$. The exhaust gas stream was passed through a 10 cm IR cell and analysed on the Fourier-transform IR instrument. Simultaneously a constant stream of the reactor solution was pumped through a 1 cm cuvette and UV/VIS spectra were recorded. In addition samples were analysed on a continuous basis in order to monitor the oxidation of $Fe^{II}L$ to $Fe^{III}L$. A typical set of IR spectra is presented in Fig. 6, from which the formation of N_2O (bands at 2224 and 1284 cm^{-1}) and the remaining NO (bands at 1876 cm^{-1}) can clearly be seen as a function of reaction time. The observed peaks were calibrated with the aid of standard mixtures of N_2O and NO introduced into the system in the absence of the reaction solution. A typical series of UV/VIS spectra recorded during such an experiment is reported in Fig. 7. The reaction is characterized by the formation of $Fe^{II}L(NO)$ (maximum at 430 nm), followed by its decomposition and formation of $Fe^{III}L$ which is accompanied by an isosbestic point at 392 nm.

The results for the formation of N_2O, the release of NO and the oxidation of Fe^{II} as a function of pH are reported in Figs. 8–11 for L = hedtra, dtpa, edta and nta, respectively. Fig. 8 indicates that NO is completely absorbed by the $Fe^{II}(hedtra)/S^{IV}$ solution at the start of the reaction, and saturation is reached after *ca.* 30 min. Subsequently the concentration of NO leaving the reactor increases but does not reach the concentration level of that entering the reactor. Notwithstanding the saturation of Fe^{II}(hedtra) by NO, 30% of the NO is still absorbed by the solution. The continuous formation of N_2O is accompanied by the oxidation of Fe^{II} to Fe^{III}. Although similar trends are observed at the investigated pH levels, some differences in for instance the $[N_2O]$ and the detailed time dependence do exist. More NO is absorbed in basic media and is accompanied by a higher concentration of NO_2. Similar results are reported for

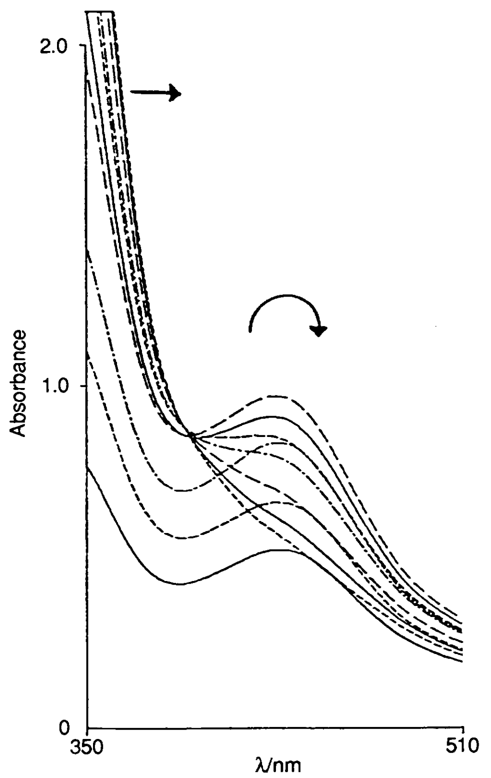


Fig. 7 Repetitive scan UV/VIS spectra of the reaction solution in the flow reactor during the reaction of NO with Fe(hedtra)–S^{IV} mixtures at pH 8.0 (Δt = 5 min)

the other complexes in Figs. 9–11. The different reactivities observed are related to the nature of the polyaminocarboxylate ligands since this on the one hand controls the lability of co-ordinated water molecules on the $Fe^{II}L$ species and on the other hand the redox potential of the $Fe^{II/III}L$ system.[7,32] The dtpa complex (Fig. 9) exhibits a remarkable property in that it is not oxidized in an alkaline medium and only very slowly oxidized in an acidic medium. This is in agreement with the lower oxidation sensitivity of this complex,[32] which can probably be related to the very effective blocking of the iron(II) centre by the dtpa ligand, such that NO will only be weakly co-ordinated and the redox reaction with sulfur(IV) oxides will not be very effective. In comparison, the edta and nta complexes are oxidized more rapidly, and the formation of $Fe^{III}L(SO_3)$ is very significant in alkaline media. At pH 5.6 the formation of FeL(NO) can clearly be seen from the UV/VIS spectra, which is then followed by the redox reaction to produce $Fe^{III}L$ and N_2O. At pH 8 the formation of the FeL(NO) species cannot be observed due to the rather rapid subsequent redox reaction. The concentration *vs.* time plots observed for the formation of N_2O suggest that this species may be stored in another form (*viz.* as nitrogen-sulfur oxides) following the reaction of FeL(NO) with sulfur(IV) oxides. Important to note is the high degree of absorption of NO in alkaline Fe^{II}(edta) solution, an aspect that has been reported in the literature[20] and may indicate an effective catalytic cycle for the reaction of NO with S^{IV}.

Overall Reaction Cycle.—An important result of this investigation for the catalytic activity of the $Fe^{II}L$ complexes is the observed relatively fast oxidation to $Fe^{III}L$ which is not capable of reacting with NO.[6,7] Although this oxidation was also observed by other investigators, even under conditions where large quantities of $HON(SO_3)_2^{2-}$ are produced,[17,18,22] no

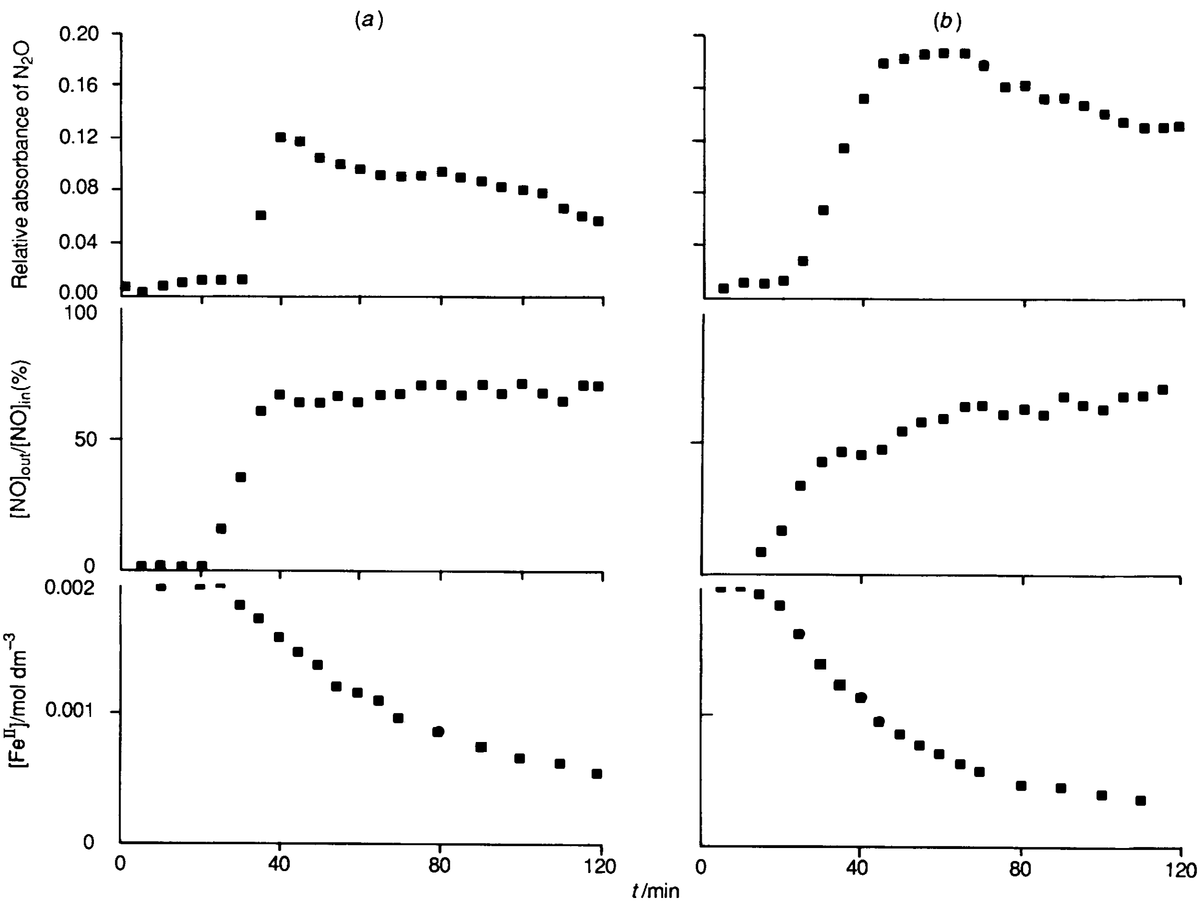


Fig. 8 Time dependence of the concentrations of Fe^{II}, NO and N_2O in the Fe(hedtra)–NO–S^{IV} system. pH 5.6 (*a*), 8.0 (*b*)

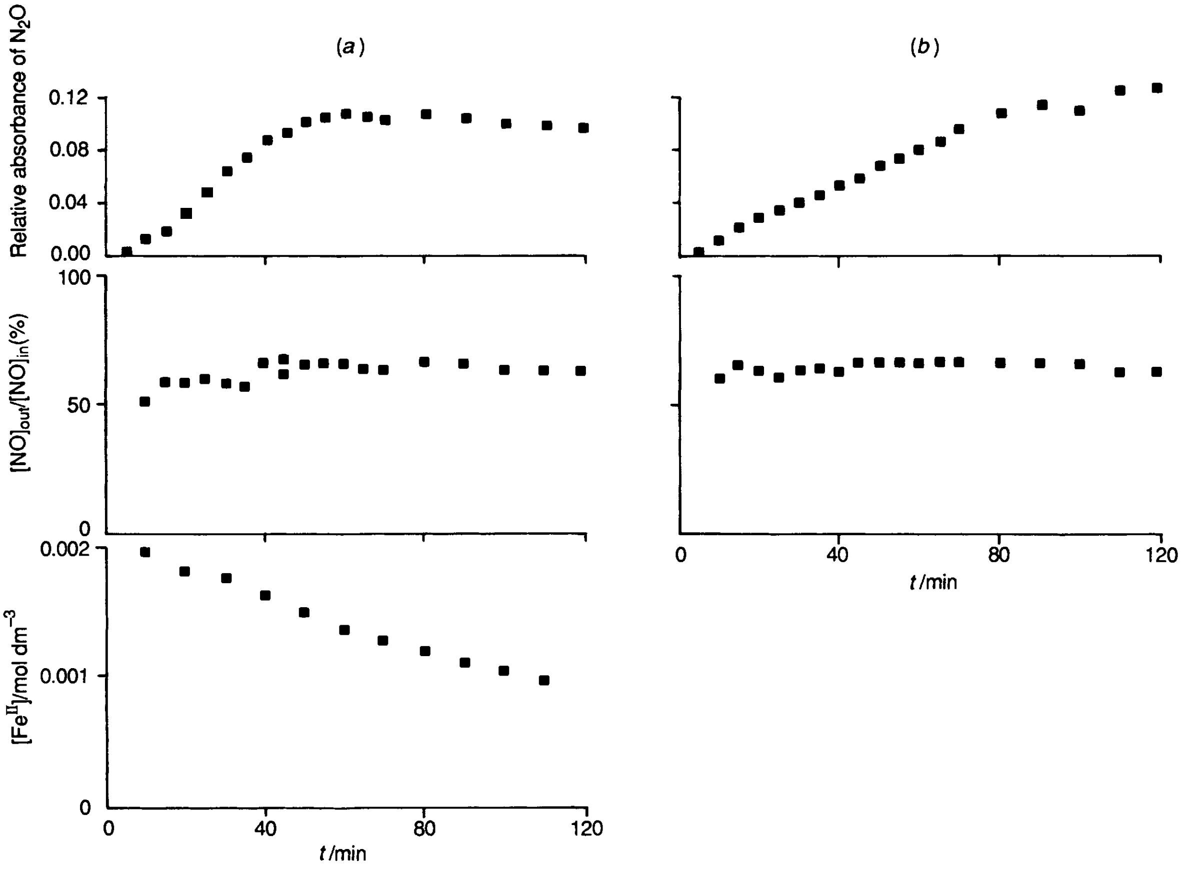


Fig. 9 Time dependence of the concentrations of Fe^{II}, NO and N_2O in the Fe(dtpa)–NO–S^{IV} system. pH 5.6 (*a*), 8.0 (no oxidation of Fe^{II}) (*b*)

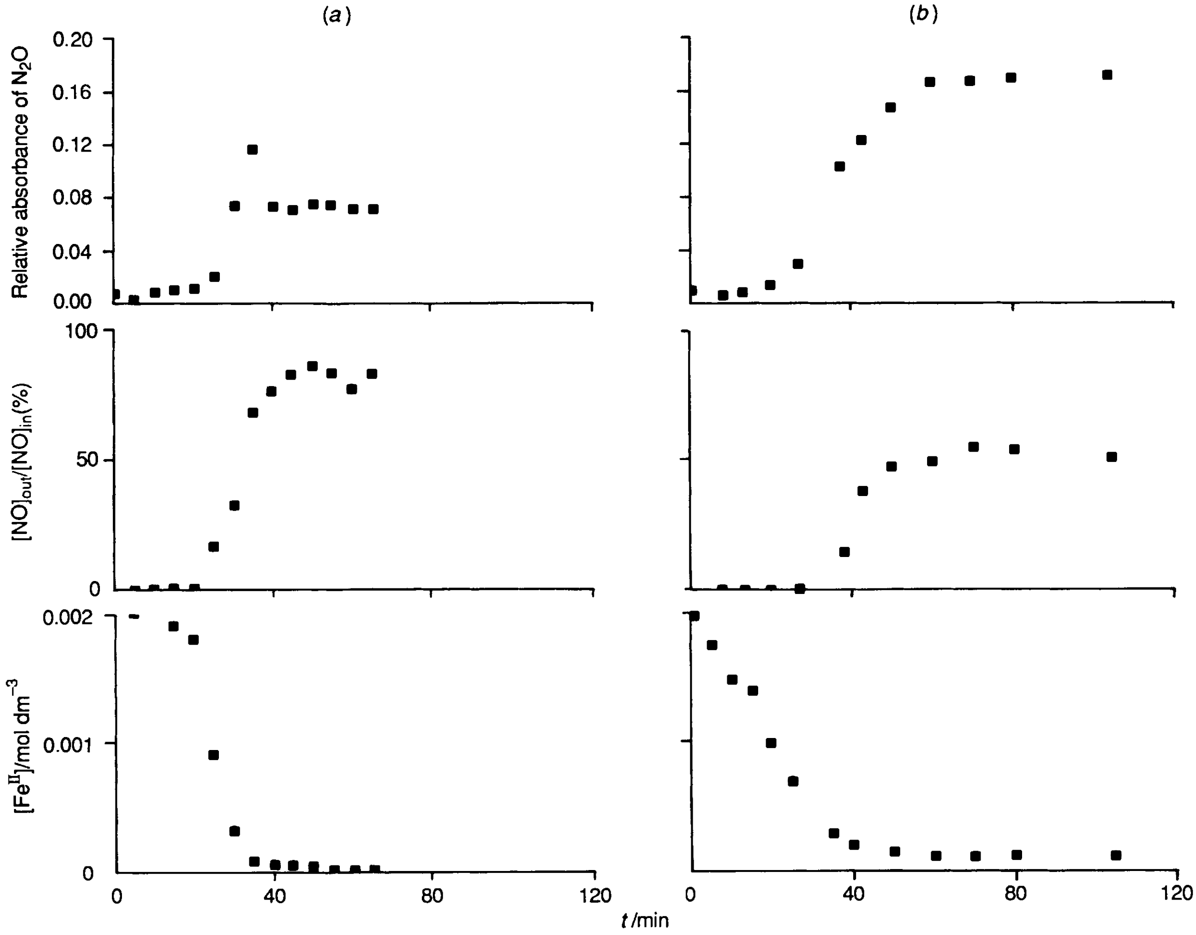


Fig. 10 Time dependence of the concentrations of Fe^{II}, NO and N_2O in the Fe(edta)–NO–S^{IV} system. pH 5.6 (*a*), 8.0 (*b*)

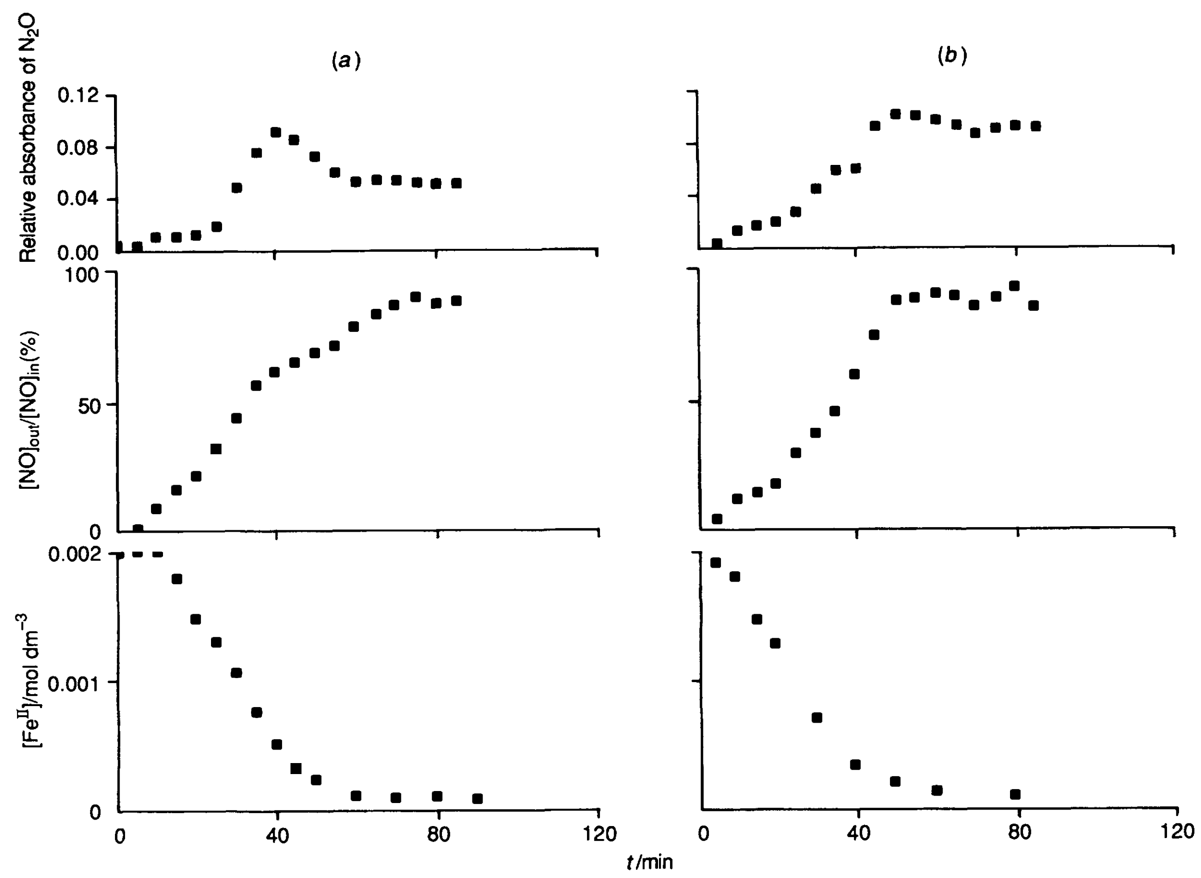


Fig. 11 Time dependence of the concentrations of Fe^{II}, NO and N_2O in the Fe(nta)–NO–S^{IV} system. pH 5.6 (*a*), 8.0 (*b*)

satisfactory explanation was offered. It is therefore important to consider alternative reaction routes that will result in the overall oxidation of the iron(II) complexes. One possibility is a sulfite-induced intramolecular redox reaction in the $Fe^{II}L(NO)$ species which could follow the reactions outlined in Scheme 4. This

$$Fe^{II}L(NO) + SO_3^{2-} \longrightarrow (SO_3)Fe^{II}L(NO)$$
$$\downarrow$$
$$(SO_3)Fe^{III}L + NO^- \text{ (i.e. } N_2O)$$

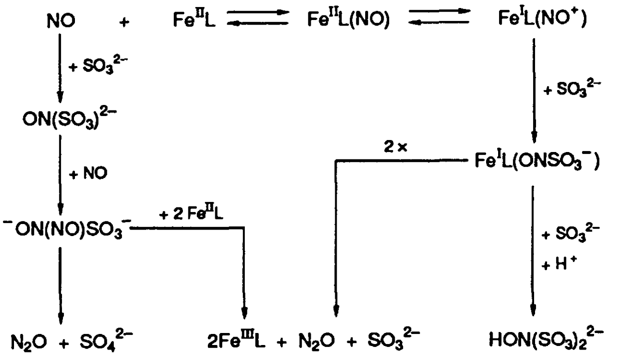
Scheme 4

means that inclusion of sulfite in the co-ordination sphere of the $Fe^{II}L(NO)$ complex could change the nature of the Fe^{II}–NO bond from Fe^{I}–NO^+ to Fe^{III}–NO^-, *via* for instance a *trans* effect of co-ordinated sulfite. Thus attack of sulfite at the metal centre could offer an alternative explanation for the formation of $Fe^{III}L$. Sulfite-induced autoxidation reactions of Fe^{II}, Co^{II} and Mn^{II} have been reported[49,50] and studied in more detail recently.[51–54] Such an induced oxidation process may involve the participation of sulfite radicals, SO_3^{-}, which could react with NO to produce $ONSO_3^{-}$ and $HON(SO_3)_2^{2-}$ as shown in Scheme 2. Another realistic possibility involves the reaction of $^{-}ON(NO)SO_3^{-}$ with $Fe^{II}L$ to produce $Fe^{III}L$, N_2O and sulfite as indicated in Scheme 5.[17,55]

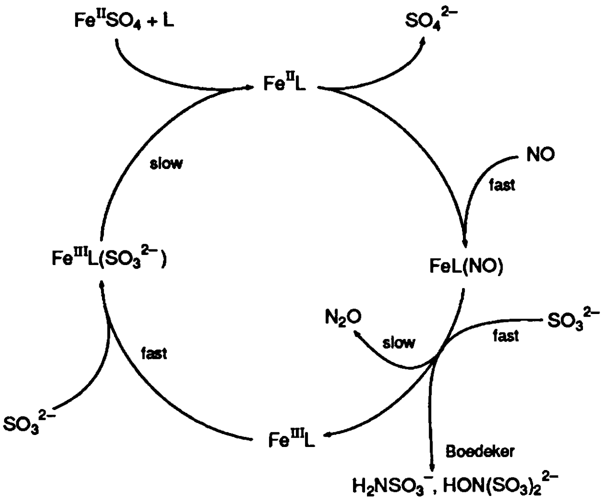
$$^{-}ON(NO)SO_3^{-} + 2Fe^{II}L \longrightarrow 2Fe^{III}L + N_2O_2^{2-} + SO_3^{2-}$$
$$\downarrow{+2H^+}$$
$$N_2O + H_2O$$

Scheme 5

The reaction routes discussed above and presented in Schemes 1–5 and equations (3) and (4) can be summarized in the overall Scheme I. Depending on the selected concentration ratio, pH and employed polyaminocarboxylate ligand L, different reaction routes can be followed. Co-ordinated NO can react as such or as NO^+ with sulfite to account for the observed decomposition reactions. The species $^{-}ON(NO)SO_3^{-}$ is especially produced in the presence of a high NO concentration, and the redox reaction with $Fe^{II}L$ occurs in a subsequent step. The nitrosyl character of co-ordinated NO can *via* the Boedeker reaction account for the formation of $HON(SO_3)_2^{2-}$. This reaction dominates at high concentrations of S^{IV} and $Fe^{II}L$, but at low NO concentrations. It follows that an essential aspect of Scheme I is the effectiveness and nature of the co-ordination of NO to the iron(II) centre, *i.e.* the value of K_1.[7] The formation of $Fe^{III}L$ products causes the catalytic nature of the process to break down, since the reduction of $Fe^{III}L$ by sulfite to reproduce the active $Fe^{II}L$ species is a slow process.[4] The overall catalytic cycle can therefore be represented by the sequence in Scheme II. Detailed analyses of the N–S reaction products, *i.e.*



Scheme I



Scheme II

$^-ON(NO)SO_3^-$, $HON(SO_3)_2^{2-}$, *etc.*, were not performed in this study, mainly because suitable analytical procedures are still lacking. Such measurements are essential to resolve the importance of the various reactions in Scheme I and the detailed reaction mechanisms. A suitable analytical procedure based on ion chromatography is presently being developed in our laboratories.[56] The atmospheric relevance of the work described in this report will also strongly depend on the outcome of such detailed analyses. Nevertheless, this study has clearly demonstrated the production of nitrous oxide during the interaction of nitric oxide and sulfite, which could be an important source of atmospheric nitrous oxide, an aspect of great concern.[57,58] In addition, the catalytic behaviour of the $Fe^{II}L$ complexes described is of fundamental importance for a liquid-membrane technique recently suggested for stack-gas scrubbing utilizing these complexes.[59]

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