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# Investigation of the redox interaction between iron(III) 5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphyrinate and aminoiminomethanesulfinic acid in aqueous solution

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Stability studies have been made on aminoiminomethanesulfinic acid [aimsa, thiourea dioxide, $(NH_2)_2CSO_2$] and the reactions of aimsa and its decomposition product (dithionite, $S_2O_4^{2-}$) with iron(III) 5,10,15,20-tetrakis-(*p*-sulfonatophenyl)porphyrinate [$Fe^{III}$(tpps)] in the presence of oxygen have been investigated. Application of NMR and stopped-flow spectrophotometry revealed direct evidence for the existence of two different forms of aimsa in aqueous solution. The slow formation of one of these forms, $NH_2NHCSO_2H$, is shown to determine the strong dependence of the reactivity of aimsa on the age of the stock solutions. Both aimsa and dithionite react in a similar way with $Fe^{III}$(tpps) in alkaline solutions. The $SO_2^{\bullet -}$ radical plays a key role in the redox reactions. The ratio of the oxygen and radical concentration determines which kind of reaction (oxidation, reduction or decomposition) will dominate. In general a high oxygen concentration and a low radical concentration favour the oxidation and decomposition of the metalloporphyrin, whereas a high radical concentration and a low oxygen concentration favour the reduction. In strongly basic solutions ([NaOH] = 0.5 M) a redox cycle between $Fe^{III}$(tpps) and $Fe^{II}$(tpps) is observed at low aimsa and dithionite concentration. Possible mechanisms for the decomposition of aimsa in alkaline solutions, as well as for the reactions between $Fe^{III}$(tpps) and aimsa or dithionite, are proposed.

Thiourea dioxide (formamidinesulfinic acid or aminoiminomethanesulfinic acid, abbreviated as aimsa) can easily be prepared *via* the oxidation of thiourea with aqueous solutions of hydrogen peroxide.[1] Numerous commercial applications are related to its strong reducing properties exhibited in alkaline solutions,[2] which are attributed to its decomposition products, mainly to sulfoxylic acid (dihydrogen dioxosulfate) $H_2SO_2$ or the anion radical $SO_2^{\bullet -}$. It is therefore widely used as a bleaching agent in the textile industry,[2,3] for reducing organo-sulfur, -selenium, -tellurium and -fluorine compounds,[4–7] as well as for the determination of some nitrogen-containing compounds[8] and metals.[9] Aminoiminomethanesulfinic acid is also a component of an effective initiation system for polymerization reactions.[10,11] Unfortunately, papers devoted to investigations of its decomposition contain many contradictory results and conclusions. It is even unknown whether the decomposition process is an ionic or a radical one.[2,9]

The present paper reports the results of stability studies on aimsa in alkaline solutions and its reaction with iron(III) 5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphyrinate $Fe^{III}$(tpps) in the presence of oxygen. This choice of oxidant is not only due to the importance of porphyrin chemistry *per se*, but also by way of comparison due to the availability of information on its reactions with other sulfur-containing reductants.[12,13] In a recent study the interaction between $Fe^{III}$(tpps) and sulfite in aqueous solution was investigated in search of evidence for redox cycling of this metalloporphyrin.[13] The application of rapid-scan spectrophotometry revealed direct evidence for such redox cycling, which was found to strongly depend on the selected experimental conditions. We have, therefore, in the present study investigated the interaction between $Fe^{III}$(tpps) and aimsa in search of conditions for redox cycling. In the case of aimsa we are dealing with a strong reducing agent, but the presence of oxygen may significantly influence its behaviour in aqueous solutions so that it could react in a similar way as in the case of sulfite/$O_2$, oxone and $H_2O_2$, where strong oxidizing conditions existed. By way of comparison, the reaction between $Fe^{III}$(tpps) and dithionite, $S_2O_4^{2-}$, a plausible decomposition product of aimsa, in the presence of oxygen was also investigated in a preliminary way.

## Experimental

Chemicals of analytical reagent grade and deionized ultrapure water were used to prepare all solutions. Nitrogen was used to deaerate solutions when required. Aqueous $HClO_4$ and NaOH were used to adjust the pH, and $NaClO_4$ to adjust the ionic strength of the test solutions. Aminoiminomethanesulfinic acid [$(NH_2)_2CSO_2$] and sodium dithionite ($Na_2S_2O_4$) were from Aldrich; $[Fe^{III}(tpps)]^{3-}$ was synthesized according to the literature.[14] 2-Cyclohexylaminoethanesulfonic acid (ches, Aldrich) or $NaHCO_3$ were used for the preparation of buffer solutions.

The UV/VIS spectra were recorded on Shimadzu UV-2102/3102PC spectrophotometers. Rapid-scan measurements were performed on a Bio Sequential SX-17MV Stopped-Flow Reaction Analyser from Applied Photophysics equipped with a J & M detector connected to a TIDAS 16-416 spectrophotometer. Stopped-flow measurements were performed on a Bio Sequential SX-18MV stopped-flow spectrophotometer. The $^1H$ NMR spectra were recorded on a 400 MHz Bruker Avance DPX-400 spectrometer at 305 K. Commercial grade deuteriated water, $D_2O$ (Aldrich, 99.9%), was used without further purification.

## Results and Discussion

### Decomposition of aimsa in alkaline media

Aminoiminomethanesulfinic acid is characterized by an absorbance maximum at 269 nm ($\varepsilon = 489$ M$^{-1}$ cm$^{-1}$[15]), such that its decomposition can be followed spectrophotometrically. The UV spectrum of an air-saturated alkaline solution of it was recorded as a function of time. The absorbance at 269 nm decreased in intensity with time in strongly alkaline solutions

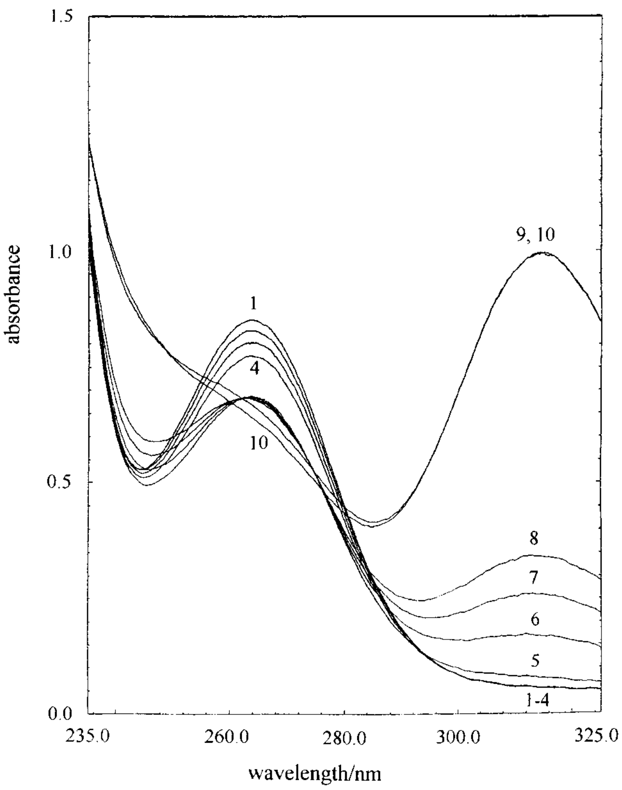


**Fig. 1** Spectral changes recorded for the decomposition of aimsa in strongly basic medium (air-saturated solutions). [aimsa] = $1.8 \times 10^{-3}$ M, [NaOH] = 0.5 M, 25 °C, $t \approx 1200$ s; $\Delta t = 1$ min for spectra 1–4, 3 min between spectrum 4 and 5, 1 min for spectra 5–8 and 5 min for the last two spectra

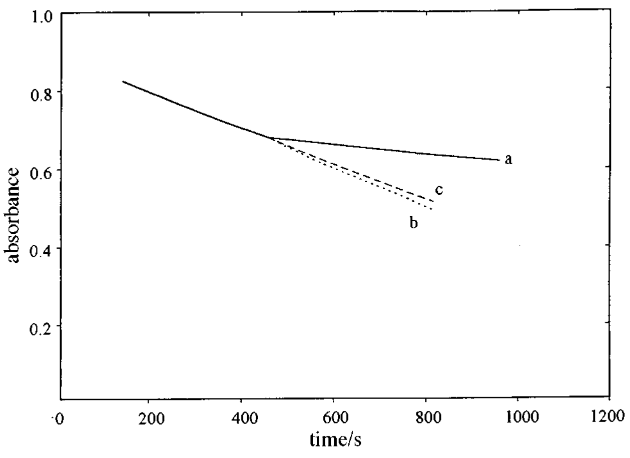


**Fig. 2** Absorbance *vs.* time traces for the decomposition of aimsa in a strongly basic medium (air-saturated solution): (a) in a sealed tandem cuvette, (b) in an open tandem cuvette and (c) after subtraction of the dithionite absorbance at 269 nm. [aimsa] = $1.8 \times 10^{-3}$ M, [NaOH] = 0.5 M, 25 °C, $\lambda = 269$ nm

([NaOH] = 0.5 M) and after some delay a band appeared at 315 nm which increased in intensity with time and reached a constant value (Fig. 1). This band is the same as that observed previously for sodium dithionite.[9] The observed absorbance *vs.* time traces at 269 and 315 nm are presented in Figs. 2 and 3, respectively. The trace at 269 nm clearly shows a peculiar break after which the absorbance decrease continues at a slower rate. If air is bubbled through the cuvette there is no break in the trace. Interestingly this break point was observed more clearly if the reaction was performed in a sealed quartz cuvette. If the cuvette was open to air only a weak break in the curve occurred. It is important to mention that the time of the break point corresponded to the time of the appearance of dithionite at 315 nm (Fig. 3). The latter also absorbs at 269 nm and this may partly affect the decrease in absorbance at 269 nm following the break point.

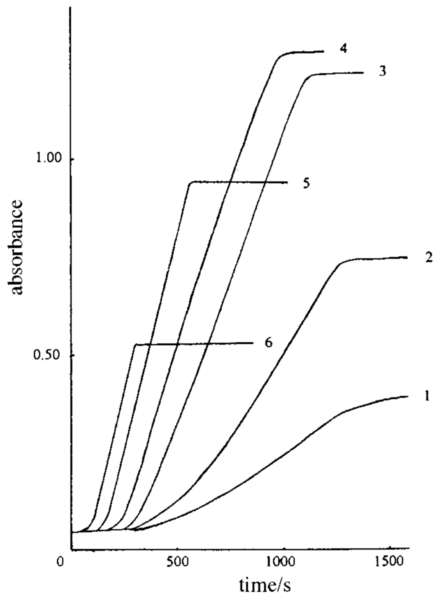


**Fig. 3** Absorbance *vs.* time traces for the decomposition of aimsa in a basic air-saturated solution: [NaOH] = 0.05 (1), 0.1 (2), 0.2 (3), 0.5 (4), 1 (5) and 2.58 M (6); [aimsa] = $1.5 \times 10^{-3}$ M, 25 °C, $\lambda = 315$ nm

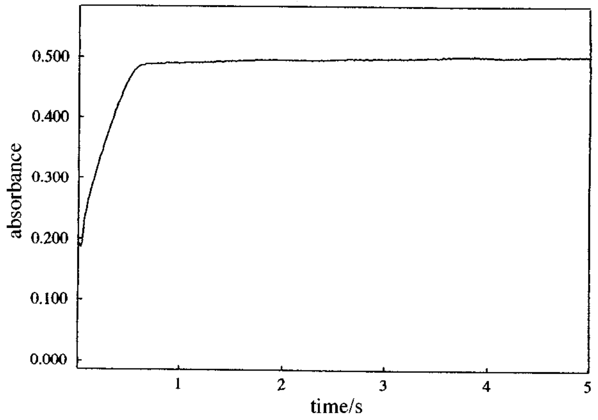


**Fig. 4** Absorbance *vs.* time trace for the decomposition of aimsa in a strongly basic nitrogen-saturated solution: [aimsa] = $1.48 \times 10^{-3}$ M, [NaOH] = 1 M, 25 °C, $\lambda = 315$ nm

In nitrogen-saturated strongly alkaline solutions the appearance of dithionite was observed immediately after mixing of an aqueous solution of aimsa with base (Fig. 4). Interestingly, we were not able to observe any increase in absorbance at 315 nm during the time range mentioned in Fig. 4 if we used a fresh nitrogen-saturated solution of aimsa (time between dissolution and the kinetic run was less than 5 min). The dependence of the aimsa reactivity on the age of the stock solution was observed earlier by Mefodieva[16] and Rabai *et al.*,[17] and a possible explanation for this observation will be given later on. In all subsequent experiments we used aged solutions of aimsa (not less than 1 h). Longer aging (up to 24 h) of aqueous (pH 4–5) solutions of aimsa had no influence on the kinetic characteristics.

It is known that dithionite exists in equilibrium with the sulfur dioxide anion radical, $S_2O_4^{2-} \longleftrightarrow 2\ SO_2^{\bullet -}$ ($K = 1.4 \times 10^{-9}$ M,[18] $k_1 = 1.7\ s^{-1}$[19]), which may form directly from aimsa.[9] The reaction of $SO_2^{\bullet -}$ with $O_2$ proceeds very rapidly ($k = 2.4 \times 10^9$ $M^{-1}\ s^{-1}$[20]). Therefore we assume that the delay in appearance of $S_2O_4^{2-}$ in air-saturated strongly alkaline solutions of aimsa is due to the reaction of $SO_2^{\bullet -}$ with oxygen. We were not able to observe an increase in absorbance at 315 nm in air-saturated solutions of aimsa ($[aimsa]_0 < 2 \times 10^{-3}$ M) at pH $\leq$ 11, but it

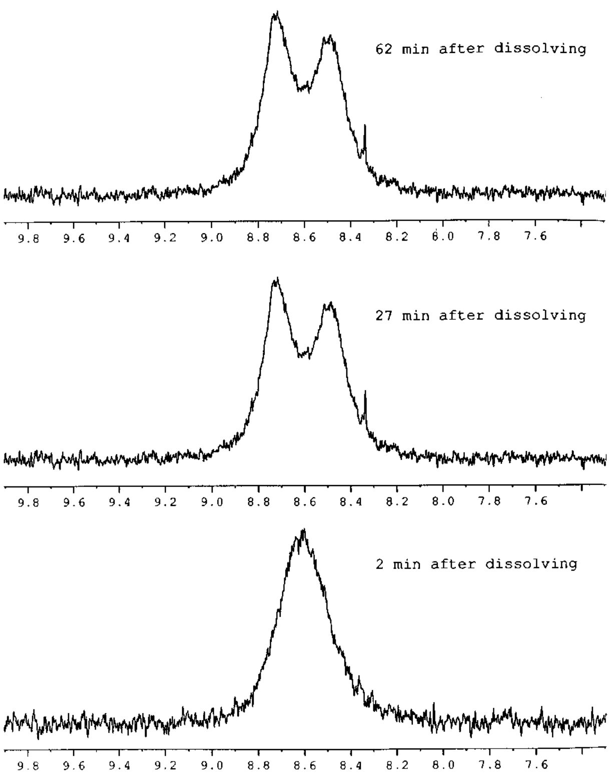
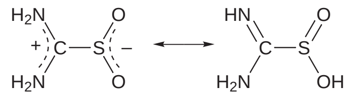


**Fig. 5** The NMR spectra recorded after dissolving aimsa in $D_2O$ (nitrogen-saturated solutions). [aimsa] ≈ 0.15 M, 30 °C

was observed in the nitrogen-saturated solutions.[21] At pH $\leqslant 11$ the absorbance at 269 nm gradually decreases to close to zero and there is no increase in absorbance at 315 nm.

Interestingly, the rate of appearance of $S_2O_4^{2-}$ does not depend on pH in strongly alkaline solutions (Fig. 3). This result can be explained on the assumption that aimsa exists in different tautomeric forms in aqueous solution, or that there is a rearrangement of it after being dissolved in water. The existence of two tautomeric forms of aimsa in aqueous solution has been assumed by many authors,[4,21] but direct experimental evidence is not available.



I II

It is known that aimsa exists in form **I** in the solid state.[22] In order to investigate possible changes in its structure after being dissolved in water, $^1H$ NMR spectra of nitrogen-saturated solutions of aimsa were recorded as a function of time. Fig. 5 shows that the initial peak at δ 8.6 quickly splits into a doublet. The changes in the NMR spectra were observed only during the first minutes after dissolving aimsa in water (the earlier investigators only observed the final doublet[23]). A reasonable explanation for the splitting into a doublet invokes a decrease in symmetry along the C–S bond, followed by intermediate exchange between two magnetically non-equivalent nitrogen nuclei. A similar splitting into a doublet was observed earlier in the NMR spectra of thiourea.[24] The absence of the $SO_2H$ proton may be explained by fast equilibration between deuteriated water and the acidic hydrogen. Unfortunately, we were not able to record any $^1H$ NMR spectra of aimsa in alkaline solutions. This may be due to the base-catalysed NH-proton exchange, since the same behaviour was observed for thiourea.[25]

Fig. 3 shows also that the absorbance increase at 315 nm exhibits good zero-order behaviour at $[OH^-] \geqslant 0.2$ M. At lower pH we observed deviations from zero-order behaviour. Such a changeover for $d[S_2O_4^{2-}]/dt$, depending on the pH, was previously observed in alkaline solutions.[9]

In order to determine the concentration of $S_2O_4^{2-}$ in aimsa solutions, $\varepsilon(S_2O_4^{2-})$ at 315 nm is required. There is a relatively large scatter in the $\varepsilon(S_2O_4^{2-})$ data in the literature ($\lambda = 315$ nm), 6900,[26,27] 8000[28] and 8043[29] $M^{-1}\ cm^{-1}$, which could be due to the effect of dissolved oxygen that will oxidize $S_2O_4^{2-}$, or the purity of dithionite. Using the most reliable value of 8043 $M^{-1}\ cm^{-1}$ (ref. 29), where analytically pure dithionite was obtained for the first time, we estimate the concentration of $S_2O_4^{2-}$ produced during aimsa decomposition in 0.5 M NaOH to be $1.5 \times 10^{-4}$ M, much smaller than the initial concentration of aimsa (Fig. 3), even taking into account the influence of oxygen. We therefore assume that there exists another, non-radical pathway for aimsa decomposition. The most plausible products of this reaction are sulfoxylate $SO_2^{2-}$ and urea (it is known that urea is a predominant nitrogen-containing product of aimsa decomposition in strongly alkaline solutions[30]).

On the basis of the results mentioned above we suggest the mechanism in equations (1)–(8) for the decomposition of aimsa

$$(NH_2)_2CSO_2 \rightleftharpoons NH_2(NH)CSO_2H \tag{1}$$

$$NH_2(NH)CSO_2H + OH^- \rightleftharpoons NH_2(NH)CSO_2^- + H_2O \tag{2}$$

$$NH_2(NH)CSO_2^- + OH^- \rightleftharpoons NH_2(NH)(OH)CSO_2^{2-} \tag{3}$$

$$NH_2(NH)(OH)CSO_2^{2-} \rightleftharpoons NHCNH\ (\text{carbodiimide}) + SO_2^{2-} + H_2O \tag{4}$$

$$NH_2(NH)(OH)CSO_2^{2-} \rightleftharpoons NH_2(NH)(OH)C^{\bullet-} + SO_2^{\bullet-} \tag{5}$$

$$NHCNH \rightleftharpoons NH_2CN \tag{6}$$

$$NH_2CN + H_2O \rightleftharpoons (NH_2)_2CO \tag{7}$$

$$2\,SO_2^{\bullet-} \rightleftharpoons S_2O_4^{2-} \tag{8}$$

in alkaline solutions. In the presence of oxygen, $SO_2^{\bullet-}$ rapidly produces $O_2^{\bullet-}$ according to reaction (9).[20] The equilibration in

$$SO_2^{\bullet-} + O_2 \longrightarrow SO_2 + O_2^{\bullet-}\ (k = 2.4 \times 10^9\ M^{-1}\ s^{-1}) \tag{9}$$

reaction (1) explains the existence of 'fast' and 'slow' steps of $S_2O_4^{2-}$ appearance during aimsa decomposition. After mixing aqueous solutions of aimsa with alkali the available reactive form **II** rapidly produces $SO_2^{\bullet-}$ and $S_2O_4^{2-}$. The rest of $S_2O_4^{2-}$ is formed much slower depending on the rate of formation of $NH_2(NH)CSO_2H$. Being the rate-determining step, reaction (1) determines the pH independence of aimsa decomposition in strongly alkaline solutions.

The most challenging phenomenon is the changeover of order in $[S_2O_4^{2-}]$ with increasing pH. This changeover may be due to attainment of steady-state conditions, where $d[S_2O_4^{2-}]/dt$ reaches a constant value. Seemingly, there is an interaction between nitrogen-containing products of radical and ionic aimsa decomposition at $[OH^-] \geqslant 0.2$ M: carbodiimide, urea and cyanamide. The formation of these compounds was observed in alkaline solutions of aimsa[30] and some of them may be formed from the nitrogen-containing radical, produced in reaction (5). The equilibration of its reactions accounts for the constant value of $d[S_2O_4^{2-}]/dt$ in strongly alkaline solutions.

### Reaction of aimsa with $Fe^{III}$(tpps) in alkaline solutions

The reaction between the $Fe^{III}$(tpps) dimer and aimsa was studied at pH 11 ($NaHCO_3$ buffer) using a tandem cuvette. In order to avoid spontaneous decomposition of aimsa before mixing with $Fe^{III}$(tpps), only the metalloporphyrin solution was buffered. After mixing the two solutions the pH was

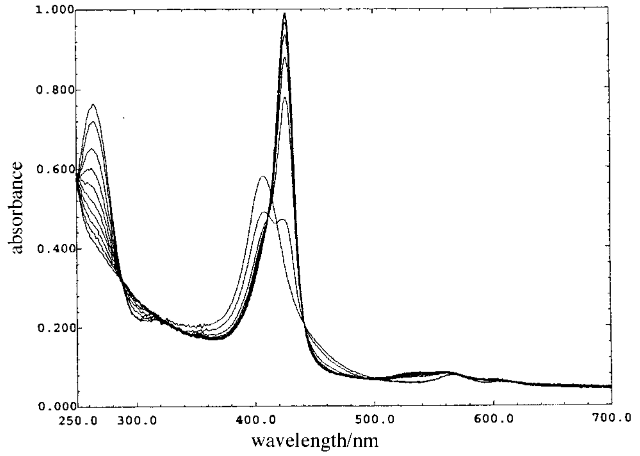


**Fig. 6** Spectral changes recorded for the reaction between the Fe$^{III}$(tpps) dimer and aimsa in a nitrogen-saturated basic solution. [Fe$^{III}$(tpps)] = 6 × 10$^{-6}$ M, [aimsa] = 7.5 × 10$^{-4}$ M, pH 11; $I$ = 0.1 M; 25 °C; $\Delta t$ = 1 min between the first two spectra and 5 min between the others

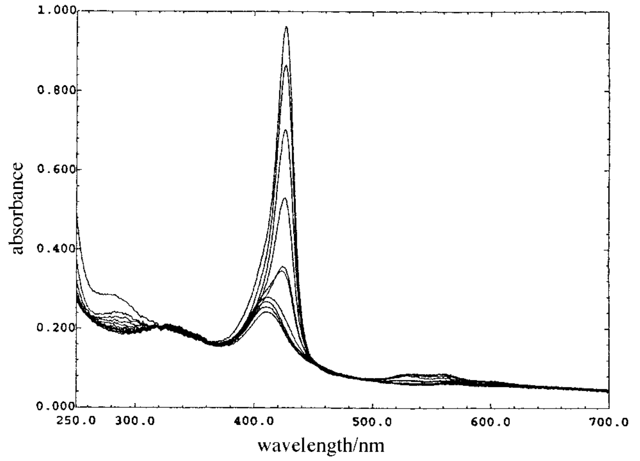


**Fig. 7** Spectral changes recorded for the back reaction between the Fe$^{III}$(tpps) dimer and aimsa in a nitrogen-saturated basic solution. Details as in Fig. 6 except $\Delta t$ = 150 min (see Discussion)

approximately 11. The aimsa and oxygen concentrations were varied, whereas the Fe$^{III}$(tpps) concentration (6 × 10$^{-6}$ M) and the ionic strength (0.1 M) were kept constant. Fig. 6 shows the spectral changes observed for the reaction of Fe$^{III}$(tpps) with a large excess of aimsa (7.5 × 10$^{-4}$ M) in nitrogen-saturated solutions. The cycle time between the first two spectra is 1 min and 5 min between the others. After 1 min a clear decrease in the Soret band of the Fe$^{III}$(tpps) dimer and the appearance of a new band at λ = 426 nm is observed (Fig. 6). Maximum absorbance of the new band is reached after approximately half an hour. These spectral changes can be assigned to the reduction of the Fe$^{III}$(tpps) dimer to the Fe$^{II}$(tpps) dimer and are in full agreement with the literature.[12,13,18,31] Following the formation of the Fe$^{II}$(tpps) band, which remains stable for about 1 h, a slow back reaction takes place and the spectral changes show that the Fe$^{II}$(tpps) band slowly decreases and after about 15 h the Fe$^{III}$(tpps) band is formed again (Fig. 7). The intensity of the Fe$^{III}$(tpps) band is low in comparison to its intensity at the beginning of the reaction, which demonstrates that, beside the back oxidation to Fe$^{III}$(tpps), decomposition of the complex also occurs. Thus three different reactions takes place: reduction of Fe$^{III}$(tpps) to Fe$^{II}$(tpps), back oxidation and overall decomposition.

In order to investigate the influence of oxygen on these reactions the same experiment was performed with air-saturated solutions. The spectral changes clearly showed that in the presence of oxygen the formation of Fe$^{II}$(tpps) is inhibited, whereas decomposition and the back reaction are accelerated. The

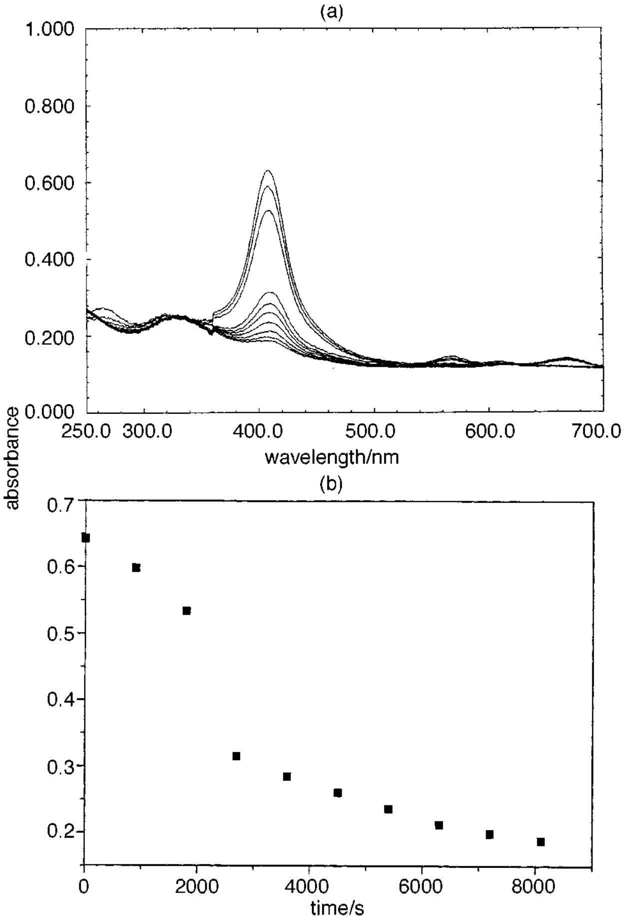


**Fig. 8** (a) Spectral changes recorded for the reaction between the Fe$^{III}$(tpps) dimer and aimsa in an air-saturated basic solution. [Fe$^{III}$(tpps)] = 6 × 10$^{-6}$ M, [aimsa] = 5 × 10$^{-5}$ M, pH 11, $I$ 0.1 M, 25 °C, $\Delta t$ = 900 s. (b) Absorbance *vs.* time dependence for the reaction between the Fe$^{III}$(tpps) dimer and aimsa in an air-saturated basic solution. [Fe$^{III}$(tpps)] = 6 × 10$^{-6}$ M, [aimsa] = 5 × 10$^{-5}$ M, pH 11, $I$ 0.1 M, 25 °C, λ = 408 nm

decay of the Soret band of the Fe$^{III}$(tpps) is larger and the intensity of the Fe$^{II}$(tpps) band is much lower than in the case of nitrogen-saturated solutions, indicating that oxygen favours the oxidation and decomposition of the complex. At high oxygen concentration the oxidation and decomposition of Fe$^{III}$(tpps) is favoured, whereas the reduction is inhibited. This can be explained by the fact that in the presence of oxygen $SO_2^{\bullet -}$, which is a product of the aimsa decomposition in alkaline solutions, rapidly produces $O_2^{\bullet -}$ according to reaction (9). We assume that $SO_2^{\bullet -}$, being a radical, reacts with biradical $O_2$ more rapidly than sulfoxylate; the same situation was observed for dithionite.[21] The radical $O_2^{\bullet -}$ is known in the literature[32] to oxidize iron(II) complexes to Fe$^{III}$ and to produce hydrogen peroxide, which is also able to oxidize Fe$^{II}$ to Fe$^{III}$, equations (10)–(12). Thus a whole range of species can be

$$Fe^{2+} + O_2^{\bullet -} + 2\,H_2O \longrightarrow Fe^{3+} + H_2O_2 + 2\,OH^- \quad (10)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (11)$$

$$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^- \quad (12)$$

formed, which can all oxidize and decompose Fe$^{III}$(tpps). The more oxygen present in solution, the more of these species can be formed.

In order to investigate the influence of aimsa on the redox reactions, the oxygen concentration was kept constant (air-saturated solutions) and the reaction between Fe$^{III}$(tpps) and aimsa was performed using different aimsa concentrations. In

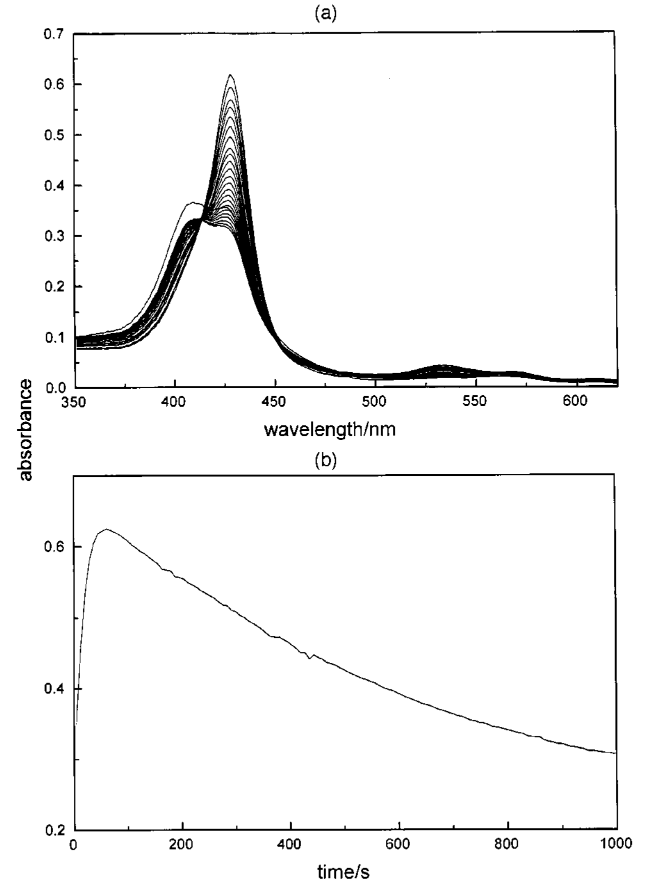


**Fig. 9** (a) Rapid-scan spectra recorded for the reaction between the $Fe^{III}$(tpps) dimer and aimsa in an air-saturated strongly basic solution. [$Fe^{III}$(tpps)] = [aimsa] = $6 \times 10^{-6}$ M, [NaOH] = 0.5 M, 25 °C, $\Delta t = 20$ s. (b) Absorbance *vs.* time trace for the reaction between the $Fe^{III}$(tpps) dimer and aimsa in an air-saturated strongly basic solution. [$Fe^{III}$(tpps)] = [aimsa] = $6 \times 10^{-6}$ M, [NaOH] = 0.5 M, 25 °C, $\lambda = 428$ nm

the case of a small increase or a small decrease in the aimsa concentration no significant change could be observed in terms of the participating redox reactions. If the aimsa concentration is however decreased significantly (from $7.5 \times 10^{-4}$ to $5 \times 10^{-5}$ M) the spectral changes show a different behaviour [Fig. 8(a) and 8(b)]. Only a decay in the Soret band of the $Fe^{III}$(tpps) dimer due to decomposition (cycle time 15 min) and no formation of the $Fe^{II}$(tpps) band are observed. Obviously the ratio between oxygen and aimsa plays an important role in the redox reactions. In this case the oxygen concentration is higher than the aimsa concentration, and the oxidation as well as decomposition of the complex is favoured. If the aimsa concentration is higher than the oxygen concentration, partial reduction of the complex can be observed along with its decomposition and back oxidation. In order to increase the concentration of radicals the same experiment was repeated in a strongly alkaline medium ([NaOH] = 0.5 M after mixing) where the decomposition of aimsa is more efficient than at pH 11. The spectral changes and the absorbance *vs.* time trace at 428 nm clearly show that, under the strongly basic conditions, redox cycling can be observed [Figs. 9(a) and 9(b)]. The formation of the $Fe^{II}$(tpps) band is fast (about 30 s) compared to the slow back oxidation [more than 1000 s; Fig. 9(b)]. This experiment demonstrates that the formation of the $SO_2^{\bullet-}$ radical during the decomposition of aimsa, as well as the ratio between the radical and oxygen concentration, determine the redox processes.

### Reaction of dithionite with $Fe^{III}$(tpps) in alkaline solutions

Similar experiments as in the case of aimsa were also performed with dithionite. In the case of nitrogen-saturated solutions (pH ≈ 11) and a large excess of dithionite ($6 \times 10^{-4}$ M), reduction of the $Fe^{III}$(tpps) dimer to the $Fe^{II}$(tpps) dimer occurs. This observation is in agreement with the literature.[12] If oxygen is added to the $Fe^{III}$(tpps)–dithionite system decomposition and oxidation of the metalloporphyrin plays a significant role. Fig. 10(a) shows the spectral changes of the reaction between $Fe^{III}$(tpps) and dithionite ($6 \times 10^{-5}$ M) in the presence of air (approximately 50% air-saturated solution). There is no formation of the $Fe^{II}$(tpps) band at $\lambda = 426$ nm, but a new band at $\lambda = 421$ nm appears for a short time and decomposes [Fig. 10(a) and 10(b)]. According to earlier results[13] this band can be assigned to the oxidation of $Fe^{III}$(tpps) to $Fe^{IV}O(tpps^{+})$ or $Fe^{V}$O(tpps). During the decomposition of the band at 421 nm a shift back towards the wavelength of the $Fe^{II}$(tpps) dimer band occurs [Fig. 10(a) and 10(b)]. At very low dithionite concentration ($6 \times 10^{-6}$ M) and in a strong alkaline medium ([NaOH] = 0.5 M) a redox cycle between $Fe^{III}$(tpps) and $Fe^{II}$(tpps) does occur [Fig. 11(a) and 11(b)] as was observed in the case of aimsa under these conditions. In agreement with the redox cycle observed for aimsa, the formation of $Fe^{II}$(tpps) is fast (approximately 30 s) whereas the back oxidation is slow [about 1000 s; Fig. 11(b)]. The intensity of the $Fe^{II}$(tpps) band observed during the redox cycling with dithionite is much lower than the $Fe^{II}$(tpps) band observed during the redox cycling with aimsa [Figs. 9(a), 9(b) and 11(a), 11(b)] indicating that more $Fe^{II}$(tpps) is formed when aimsa is used.

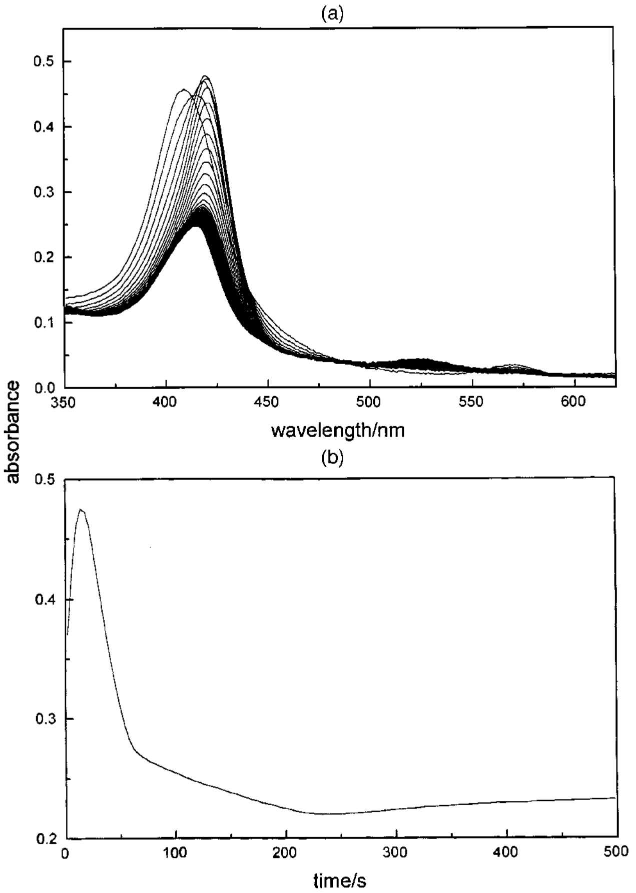


**Fig. 10** (a) Rapid-scan spectra recorded for the reaction between the $Fe^{III}$(tpps) dimer and dithionite in a basic solution in the presence of air. [$Fe^{III}$(tpps)] = $6 \times 10^{-6}$ M, [$S_2O_4^{2-}$] = $6 \times 10^{-5}$ M, pH 11; $I = 0.1$ M, 25 °C, $\Delta t = 4$ s. (b) Absorbance *vs.* time trace for the reaction between the $Fe^{III}$(tpps) dimer and dithionite in basic solution in the presence of air. [$Fe^{III}$(tpps)] = $6 \times 10^{-6}$ M, [$S_2O_4^{2-}$] = $6 \times 10^{-5}$ M, pH 11, $I = 0.1$ M, 25 °C, $\lambda = 421$ nm

## Conclusion

The experiments show that both aimsa and dithionite react in a very similar way with $Fe^{III}$(tpps) in alkaline solutions.

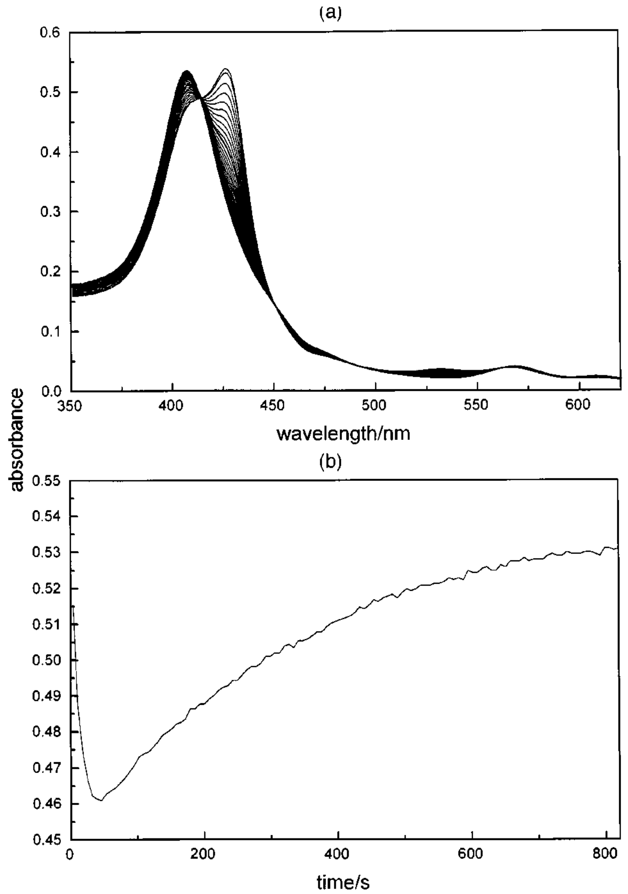


**Fig. 11** (a) Rapid-scan spectra recorded for the reaction between the $Fe^{III}$(tpps) dimer and dithionite in an air-saturated strongly basic solution. $[Fe^{III}(tpps)] = [S_2O_4^{2-}] = 6 \times 10^{-6}$ M, [NaOH] = 0.5 M, 25 °C, $\Delta t \approx 20$ s. (b) Absorbance *vs.* time trace for the reaction between the $Fe^{III}$(tpps) dimer and dithionite in an air-saturated strongly basic solution. $[Fe^{III}(tpps)] = [S_2O_4^{2-}] = 6 \times 10^{-6}$ M, [NaOH] = 0.5 M, 25 °C, $\lambda = 406$ nm

Obviously the $SO_2^{\bullet-}$ radical plays a key role during the redox reactions. The ratio of the oxygen and radical concentrations determines which reaction (oxidation, reduction or decomposition) will dominate. In general a high oxygen concentration and a low radical concentration favour the oxidation and decomposition of the metalloporphyrin, whereas high concentrations of radicals and low oxygen concentration favour the reduction. In strong basic solutions ([NaOH] = 0.5 M) a redox cycle between $Fe^{III}$(tpps) and $Fe^{II}$(tpps) was observed at low aimsa and dithionite concentration.

The proposed mechanism for the reaction between $Fe^{III}$(tpps) and aimsa consists of reactions (1), (2), (5) and (8)–(14). The

$$(NH_2)_2CSO_2 \rightleftharpoons NH_2(NH)CSO_2H \quad (1)$$

$$NH_2(NH)CSO_2H + OH^- \rightleftharpoons NH_2(NH)CSO_2^- + H_2O \quad (2)$$

$$NH_2(NH)(OH)CSO_2^{2-} \rightleftharpoons NH_2(NH)(OH)C^{\bullet-} + SO_2^{\bullet-} \quad (5)$$

$$2\,SO_2^{\bullet-} \rightleftharpoons S_2O_4^{2-} \quad (8)$$

$$SO_2^{\bullet-} + HO_2^- \longrightarrow \text{products } (k = 5.9\ \mathrm{M^{-1}\,s^{-1}}\,{}^{33}) \quad (13)$$

$$Fe^{3+} + SO_2^{\bullet-} \longrightarrow Fe^{2+} + SO_2 \quad (14)$$

$$SO_2^{\bullet-} + O_2 \longrightarrow SO_2 + O_2^{\bullet-} \ (k = 2.4 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}) \quad (9)$$

$$Fe^{2+} + O_2^{\bullet-} + 2\,H_2O \longrightarrow Fe^{3+} + H_2O_2 + 2\,OH^- \quad (10)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (11)$$

$$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^- \quad (12)$$

rate determining step will be the decomposition of aimsa to form the $SO_2^{\bullet-}$ radicals. The last four reactions are important when oxygen is present (especially in excess) and can account for the oxidation and decomposition of the metalloporphyrin.

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