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Mechanistic insight from rapid-scan stopped-flow spectrophotometry into the autoxidation of ascorbate catalysed by an iron porphyrin complex

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The reaction of the water-soluble complex Fe^{III}(tpps) [tpps = 5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphyrinate] with ascorbic acid has been investigated in aqueous solution by a combination of rapid-scan and stopped-flow techniques. The spectral changes recorded for the reaction between the Fe^{III}(tpps) monomer and ascorbic acid in a weakly acidic medium suggest the formation of the Fe^{III}(tpps$^{\bullet+}$) radical cation and the partial formation of Fe^{II}(tpps), which depend on the concentration ratio of ascorbic acid and oxygen. In a basic medium the Fe^{III}(tpps) dimer is reduced to Fe^{II}(tpps), showing an induction period which depends on the oxygen concentration of the solution. Measurements with an oxygen-sensitive electrode clearly demonstrated that during the induction period oxygen is used up by ascorbate and that the decrease in oxygen concentration is accelerated by the presence of Fe^{III}(tpps), thus demonstrating the catalytic effect of the metalloporphyrin on the autoxidation of ascorbate. This suggests that in the presence of Fe^{III}(tpps) a redox cycle takes place [$Fe^{II/III}$(tpps)] which consumes oxygen, with the result that no spectral changes are observed during the induction period.

There is an increasing awareness of the important role of high-oxidation-state metal complexes of iron, manganese, nickel and chromium in catalytic oxidations by molecular oxygen and hydrogen peroxide. Such reactions include the oxidation of sulfite and other pollutants, epoxidation of olefins, hydroxylation of alkanes, metabolization of drugs and cleavage of DNA.[1–10] For instance reactive oxo-iron(IV/V) and -manganese(IV/V) intermediates are of increasing importance in biochemical catalytic cycles involving cytochrome P450, methane monooxygenase, ribonucleotide reductase and heme peroxidases.[9,10] In most of these systems N_4 macrocycles, such as porphyrins and peptides, are employed as non-participating ligands to stabilize such unusually high oxidation states in aqueous solution.

Spectroelectrochemical and rapid-scan UV/VIS techniques have in recent years been employed very successfully to detect such high-oxidation-state intermediates and to study their kinetic and mechanistic behaviour.[4,5,9] These measurements revealed direct evidence for the earlier suggested redox cycling of the catalyst, which forms an essential part of the overall catalytic cycle. It is in particular the redox cycling of such metal ions and complexes that has interested us over the last few years, due to their role in catalysed atmospheric oxidation processes[11] involving sulfur, nitrogen and mixed sulfur–nitrogen oxides.[12–18]

One of the water-soluble metalloporphyrins, the iron(III) 5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphyrinate [abbreviated Fe^{III}(tpps)], is known to function as a catalyst for the electrocatalytic reduction of HSO_3^- to H_2S[19] and for the electrocatalytic oxidation of sulfite to sulfate.[5] In a recent study we have investigated the interaction between Fe^{III}(tpps) and sulfite in aqueous solution in search of evidence for redox cycling of this metalloporphyrin.[20] In addition, other redox partners such as ozone, $KHSO_5$, H_2O_2, and mixed S–N oxides were also investigated in a preliminary way. The application of rapid-scan spectrophotometry has revealed direct evidence for such redox cycling ($Fe^{II/III}$ and $Fe^{III/IV}$), which strongly depends on the experimental conditions and redox partner selected.[20]

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It is known that ascorbic acid is able to reduce iron(III) complexes. The kinetics and mechanism of the oxidation of ascorbic acid by aquated iron(III) ions and complexes[21,22] as well as by the water-soluble ferriporphyrin iron(III) 5,10,15,20-tetrakis(*N*-methyl-4-pyridinio)porphyrin[23,24] have been investigated. The metal ion and metal chelate catalysed oxidation of ascorbic acid by molecular oxygen was studied by Taqui Khan and Martell[25] in an acidic medium; the catalytic activity of iron(III) species was demonstrated and compared with that of Cu^{II}.

In the present study we have investigated the reaction between Fe^{III}(tpps) and ascorbic acid in the presence of oxygen in aqueous solution in search of evidence for redox cycling of the metal complex and for the catalytic role of Fe^{III}(tpps) in the oxidation of ascorbic acid. A combination of rapid-scan spectrophotometry and stopped-flow measurements was employed.

Experimental

Chemicals of analytical reagent grade (Merck and Aldrich) and deionized Millipore water were used to prepare all solutions. Argon or 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. The Na_3[Fe^{III}(tpps)] complex was synthesized according to the literature[26] and the purity checked by UV/VIS spectrophotometry.

The UV/VIS spectra were recorded on a HP 8452A diode-array spectrophotometer or on a Shimadzu UV-2102/3102PC spectrophotometer. Rapid-scan measurements were performed in 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. Oxygen measurements were performed with an oxygen-detection system from Biolytik; details on procedures and equipment used are given elsewhere.[27]

Spectroelectrochemical experiments were carried out employing a Perkin-Elmer Lambda 9 spectrophotometer. Data acquisition was performed with the PECS software package on an Acer 910 personal computer, and an Amel 550 potentiostat/

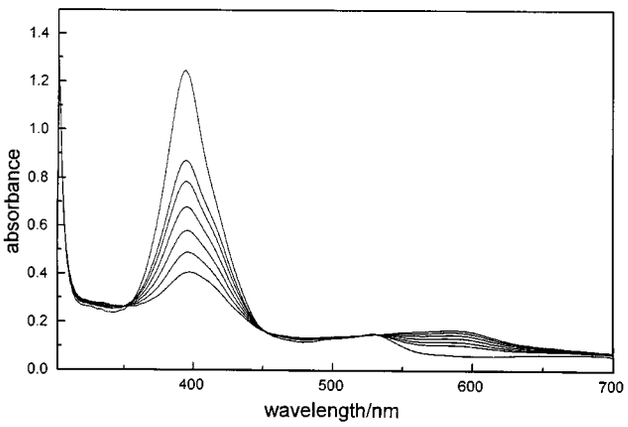

Fig. 1 Spectral changes recorded for the reaction between the Fe^{III}(tpps) monomer and ascorbic acid in Ar-saturated acidic solutions. $[Fe^{III}(tpps)] = 1 \times 10^{-5}$ M, [ascorbic acid] $= 5 \times 10^{-3}$ M, pH 5, 25 °C, $I = 0.1$ M, $\Delta t = 40$ min

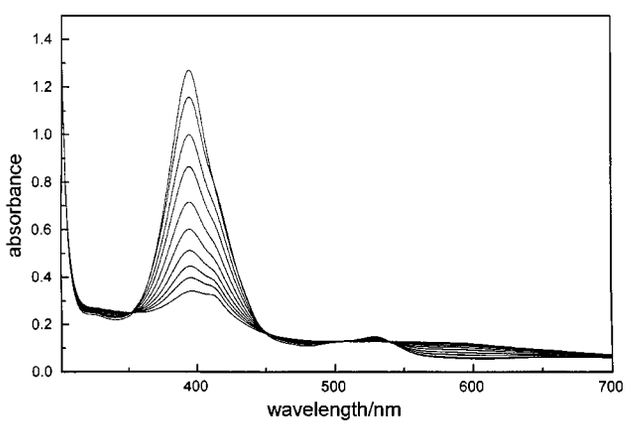

Fig. 2 Spectral changes recorded for the reaction between the Fe^{III}(tpps) monomer and ascorbic acid in air-saturated acidic solutions. Conditions as in Fig. 1 except $\Delta t \approx 2.5$ min

galvanostat was used. Details on the spectrochemical cell are given elsewhere.[28]

Results and Discussion

Reaction of Fe^{III}(tpps) with ascorbic acid at pH 5

It is known that Fe^{III}(tpps) exists as a monomer in acidic solutions, whereas in basic solutions the μ-oxo dimer is formed.[26] Short- and long-time measurements on the reaction between Fe^{III}(tpps) and ascorbic acid were performed in acidic (pH 5, monomeric species) as well as in basic media (pH 11, dimeric species). First, long-time experiments were performed at pH 5 using a tandem cuvette. The ascorbic acid and oxygen concentrations were varied whereas the Fe^{III}(tpps) concentration (1×10^{-5} M) and the ionic strength (0.1 M) remained constant. Fig. 1 shows the spectral changes observed during the reaction of Fe^{III}(tpps) with a large excess of ascorbic acid ($[H_2A] = 5 \times 10^{-3}$ M) in Ar-saturated solutions. The cycle time between each consecutive spectrum is 40 min. The Soret band of the Fe^{III}(tpps) monomer at 395 nm decreases which is typical for the oxidation of the complex to the $Fe^{III}(tpps^{\bullet+})$ radical cation. If Fe^{III}(tpps) is electrochemically oxidized, the Soret band decreases in intensity without the formation of a new band at longer wavelengths. According to the literature[29] this is due to the formation of the $Fe^{III}(tpps^{\bullet+})$ radical cation. However, there is some peak broadening in Fig. 1, indicating that partial formation of Fe^{II}(tpps) does occur. If the same experiment is repeated in air-saturated solutions similar spectral changes (decrease of the Soret band) are observed but the decay is much faster (see Fig. 2; cycle time between each consecutive spectrum is *ca.* 3 min). In addition the peak broadening can be seen much better. Obviously oxygen favours oxidation of the Fe^{III}(tpps) monomer to the $Fe^{III}(tpps^{\bullet+})$ radical cation and the partial formation of Fe^{II}(tpps) which is characterized by a peak at 425 nm.[25] A decrease in the ascorbic acid concentration (from 5×10^{-3} to 5×10^{-4} M) resulted in a slower decay of the Soret band.

Following these long-time measurements of the reaction between Fe^{III}(tpps) and ascorbic acid short-time measurements were performed. A rapid-scan spectrophotometric technique, coupled to a stopped-flow instrument, enabled the recording of UV/VIS spectra on a millisecond timescale. In a typical experiment the total measurement time was 10.5 s and the cycle time between each consecutive spectrum was 42 ms. A total of 250 spectra were recorded. The recorded spectra showed that there were nearly no spectral changes and thus no redox cycling under these conditions. The observed trends for the reaction between the Fe^{III}(tpps) monomer and ascorbic acid are very similar to those observed for the reaction between the Fe^{III}(tpps) monomer and sulfite ions.[20] In both cases only oxidation of the Fe^{III}(tpps) monomer to the $Fe^{III}(tpps^{\bullet+})$ radical cation and partial formation of Fe^{II}(tpps) were observed, but clearly no redox cycling. As in the case of sulfite, radicals must be responsible for the observed reactions.

At pH 5 the monodeprotonated ascorbate anion (HA^-) is the main species in solution and is a much stronger reductant than ascorbic acid (H_2A) itself.[22] The sequence of reactions (1)–(5)

$$Fe^{III}(tpps) + HA^- \longrightarrow Fe^{II}(tpps) + HA \quad (1)$$

$$HA + Fe^{III}(tpps) \longrightarrow Fe^{II}(tpps) + H^+ + A \quad (2)$$

$$HA + O_2 \longrightarrow H^+ + A + O_2^- \quad (3)$$

$$Fe^{II}(tpps) + O_2 \longrightarrow Fe^{III}(tpps) + O_2^- \quad (4)$$

$$Fe^{III}(tpps) + O_2^- \longrightarrow Fe^{III}(tpps^{\bullet+}) + O_2^{2-}\ (O_2^{2-} + 2\,H^+ \longrightarrow H_2O_2) \quad (5)$$

can account in a qualitative way for the observed spectral changes under these experimental conditions. Here Fe^{III}(tpps) is reduced by either HA^- or the ascorbate radical (HA) to Fe^{II}(tpps). The ascorbate radical can also be oxidized by dissolved oxygen to dehydroascorbic acid (A) in reaction (3). The produced Fe^{II}(tpps) in reactions (1) and (2) is extremely oxygen sensitive, such that reaction (4) will lead to Fe^{III}(tpps) and superoxide. The superoxide formed in (3) and (4) is able to oxidize the tpps ligand to the cation radical $tpps^{\bullet+}$. Such oxidation reactions usually result in the formation of monoimine complexes or rupture of the porphyrin chelate.[30,31] The hydrogen peroxide produced in reaction (5) can in principle oxidize Fe^{II}(tpps) to Fe^{III}(tpps), Fe^{III}(tpps) to Fe^{IV}(tpps), and tpps to $tpps^{\bullet+}$, or HA^- and HA to A. Evidence for the formation of Fe^{IV}(tpps) or Fe^{IV}(O)($tpps^{\bullet+}$) during the reaction of Fe^{III}(tpps) with H_2O_2 was reported recently.[20]

The formation of $Fe^{III}(tpps^{\bullet+})$ strongly depends on the oxygen concentration in solution which can account for the large difference in decomposition rate observed in Figs. 1 and 2. The decomposition rate will also strongly depend on the concentration of HA^-, since this is needed to initiate the overall reaction sequence. The spontaneous oxidation of HA^- by oxygen is too slow under these conditions[25] to compete with the reactions outlined above. Although redox cycling of the Fe^{III}(tpps) complex is suggested to occur in reactions (1) to (4), no direct observation of this process could be achieved, notwithstanding the fact that various concentration ratios of HA^- and O_2 were tested.

Reaction of Fe^{III}(tpps) with ascorbate anion at pH 11

Analogous measurements were performed at pH 11 with the

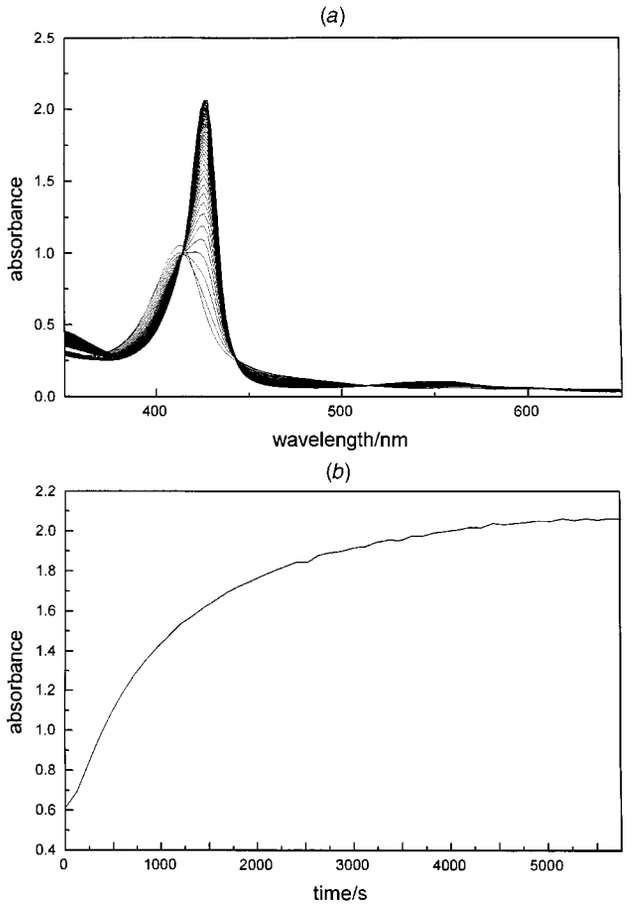

Fig. 3 (*a*) Spectral changes recorded for the reaction between the Fe^{III}(tpps) dimer and ascorbate in Ar-saturated basic solutions. [Fe^{III}(tpps)] = 1×10^{-5} M, [ascorbate] = 5×10^{-3} M, pH 11, 25 °C, $I = 0.1$ M, $\Delta t = 120$ s. (*b*) Absorbance *vs.* time trace for the reduction of the Fe^{III}(tpps) dimer by ascorbate in Ar-saturated basic solution. $\lambda = 428$ nm; other conditions as in (*a*)

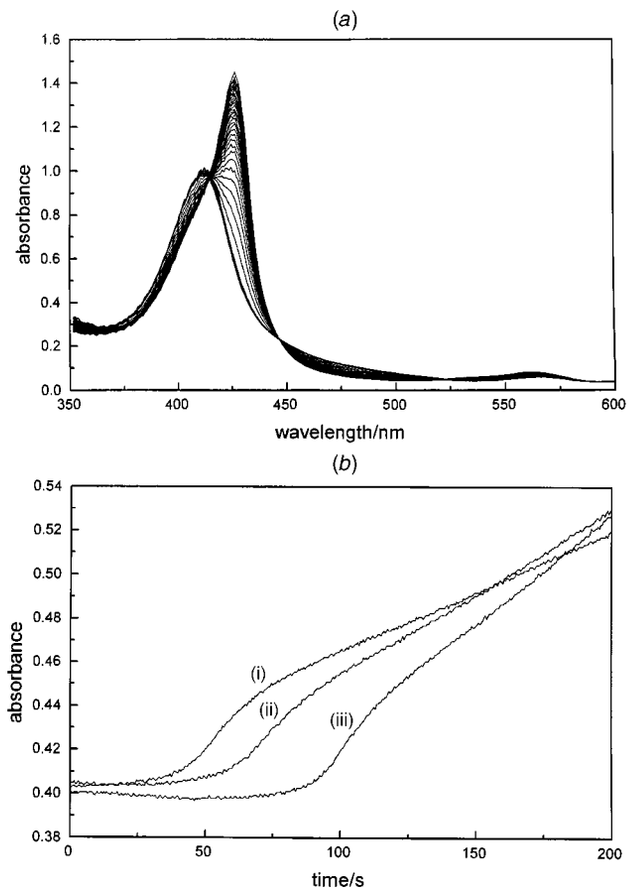

Fig. 4 (*a*) Rapid-scan spectra recorded for the reaction between the Fe^{III}(tpps) dimer and ascorbate in Ar-saturated basic solutions [Fe^{III}(tpps)] = 1×10^{-5} M, [ascorbate] = 5×10^{-3} M, pH 11, 25 °C, $I = 0.1$ M, $t = 1000$ s, $\Delta t = 20$ s. (*b*) Induction period observed for the reaction between the Fe^{III}(tpps) dimer and ascorbate in basic solutions as a function of oxygen concentration. The oxygen concentration of the Fe^{III}(tpps) solution was varied (by bubbling air/oxygen, and nitrogen-saturated ascorbate solutions were used. [Fe^{III}(tpps)] = 1×10^{-5} M, [ascorbate] = 5×10^{-3} M, pH 11, 25 °C, $I = 0.1$ M, $\lambda = 430$ nm. (*i*) Nitrogen-saturated solution (after mixing), (*ii*) 50% air-saturated solution (after mixing) and (*iii*) 50% oxygen-saturated solution (after mixing)

μ-oxo dimer of Fe^{III}(tpps) and the fully deprotonated ascorbate anion (A^{2-}). First a long-time experiment was performed using the same experimental conditions as used at pH 5 {*i.e.* [Fe^{III}(tpps)] = 1×10^{-5} M, [H_2A] = 5×10^{-3} M, $I = 0.1$ M, argon-saturated solutions}. Fig. 3(*a*) clearly shows the formation of the Fe^{II}(tpps) band at $\lambda = 426$ nm. The absorbance *vs.* time trace at $\lambda = 428$ nm demonstrates that the reduction of the Fe^{III}(tpps) dimer by ascorbate is slow [Fig. 3(*b*)]. A redox cycle can be initiated by opening the cuvette, which results in immediate reoxidation of Fe^{II}(tpps) to Fe^{III}(tpps) by oxygen from the air. The change in pH from 5 to 11, and thus in the nature of the Fe^{III}(tpps) species, has a drastic effect on the reaction with ascorbate. At pH 5 mainly oxidation of the Fe^{III}(tpps) monomer to the Fe^{III}(tpps$^{\bullet+}$) radical cation could be observed, whereas at pH 11 mainly reduction of the Fe^{III}(tpps) dimer to the Fe^{II}(tpps) species occurs under the same concentration conditions. This is most probably related to the stronger reducing ability of A^{2-} as compared to those of HA^- and H_2A.[22] It should also be considered that the co-ordinated water molecules on the μ-oxo dimer of Fe^{III}(tpps) are expected to be significantly more labile than on the monomer, which could accelerate an inner-sphere electron-transfer reaction and promote the redox process.

Following the long-time measurement of the reduction of the Fe^{III}(tpps) dimer by ascorbate anion in argon/nitrogen-saturated solutions, the same reaction was reinvestigated on a fast timescale. First 250 spectra were recorded in 10.5 s, but no spectral changes could be observed [no formation of the Fe^{II}(tpps) band at $\lambda = 426$ nm]. However, if the timescale is increased from 10.5 to 1000 s, the slow formation of Fe^{II}(tpps) can be observed following an induction period of *ca.* 30 s during which no change in absorbance occurs [Fig. 4(*a*)]. The absorbance *vs.* time traces at 430 nm [Fig. 4(*b*)] clearly show that the observed induction period depends on the oxygen concentration; the higher the oxygen concentration, the longer is the induction period.

In another series of experiments the reaction of a Fe^{II}(tpps)–ascorbate solution [Fe^{III}(tpps) was reduced with a large excess of ascorbate in nitrogen-saturated solutions] with an aqueous solution containing different oxygen concentrations was investigated. Since the formed Fe^{III}(tpps) is again reduced by ascorbate, an induction period can be seen that depends on the oxygen concentration (Fig. 5). The higher the oxygen concentration, the longer is the induction period. Although the same trends are observed in both Figs. 4(*b*) and 5, the induction periods obtained for the reduction of Fe^{III}(tpps) by ascorbate are longer compared to those obtained for the reaction between Fe^{II}(tpps)–ascorbic acid and water. In addition, in the second case the formation of Fe^{II}(tpps) is more effective since the absorbance increase following the induction period is significantly larger [compare Figs. 4(*b*) and 5]. The shape of the absorbance *vs.* time traces indicates that in both cases some autocatalytic behaviour occurs [Figs. 4(*b*) and 5].

The experiments performed show that the reduction of the Fe^{III}(tpps) dimer by ascorbate does not take place immediately, but that there is an induction period which depends on the

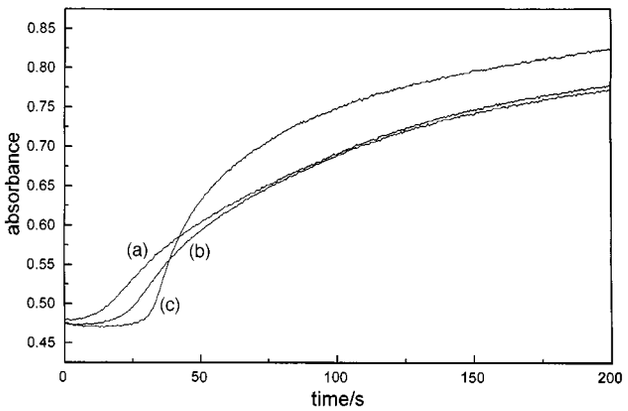

Fig. 5 Induction period observed for the reaction between the Fe^{II}-(tpps) dimer–ascorbate and basic water solutions as a function of oxygen concentration. The oxygen concentration of the Fe^{II}(tpps)–ascorbate solution was constant (nitrogen saturated) and the oxygen concentration of the water solution was varied. $[Fe^{II/III}(tpps)] = 1 \times 10^{-5}$ M, [ascorbate] = 5×10^{-3} M, pH 11, 25 °C, $I = 0.1$ M, $\lambda = 430$ nm. (*a*) Nitrogen-saturated solution (after mixing), (*b*) 50% air-saturated solution (after mixing) and (*c*) 50% oxygen-saturated solution (after mixing)

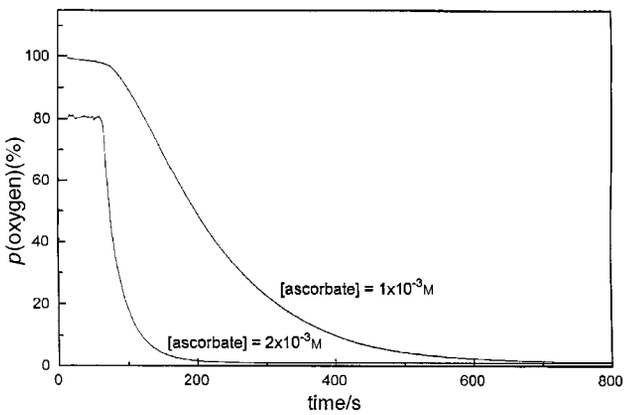

Fig. 6 Oxygen consumption of a basic air-saturated ascorbate solution as a function of ascorbate concentration in the absence of Fe^{III}(tpps). pH 11, 25 °C, $I = 0.1$ M

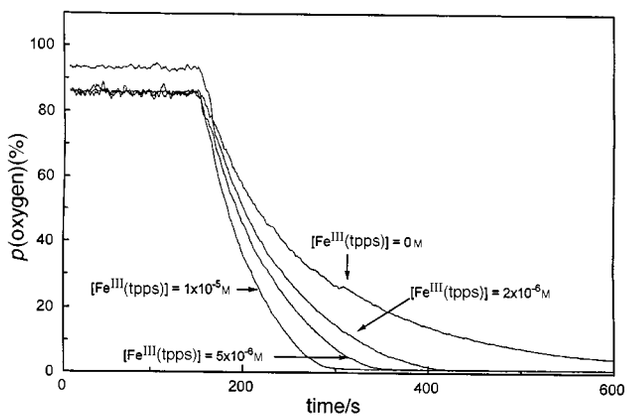

Fig. 7 Oxygen consumption of a basic air-saturated ascorbate solution as a function of Fe^{III}(tpps) concentration. [ascorbate] = 1×10^{-3} M, pH 11, 25 °C, $I = 0.1$ M

oxygen concentration. This fact strongly suggests that during the induction period redox cycling of the Fe(tpps) complex takes place, because Fe^{II}(tpps) can only be formed in the absence of oxygen [Fe^{II}(tpps) is extremely oxygen sensitive]. This means that during the induction period oxygen must be used up. This presumably occurs during the redox cycling. The Fe^{III}(tpps) is reduced by ascorbate present in high excess. The oxygen present in solution reoxidizes the Fe^{II}(tpps) rapidly to Fe^{III}(tpps), which is again reduced by ascorbate. The oxidation of Fe^{II}(tpps) to Fe^{III}(tpps) continues as long as there is oxygen present in solution. The more oxygen present, the longer the redox cycle will continue and the longer the induction period will be. Once the oxygen is used up then only reduction of Fe^{III}(tpps) to Fe^{II}(tpps) will occur. The faster the usage of oxygen, the shorter is the induction period and thus the redox cycle is complete. This can be seen from the fact that if a Fe^{II}(tpps)–ascorbate solution is used the induction period is much shorter than in the case where Fe^{III}(tpps) is used, since the Fe^{II}(tpps) will immediately be oxidized and decrease the oxygen concentration.

The redox cycling described above can be presented by the overall reactions of (6) and (7), which are both suggested to

$$[Fe^{III}(tpps)]_2O + A^{2-} \longrightarrow 2\,Fe^{II}(tpps) + A + O^{2-} \quad (6)$$
$$(O^{2-} + H^+ \rightleftharpoons OH^-)$$

$$2\,Fe^{II}(tpps) + O_2 \longrightarrow 2\,Fe^{III}(tpps) + O_2^{2-}$$
$$(O_2^{2-} + H^+ \rightleftharpoons HO_2^-)$$
$$\downarrow +OH^-$$
$$[Fe^{III}(tpps)]_2O + H^+ \quad (7)$$

involve two one-electron transfer steps during which A^{2-} (fully deprotonated ascorbic acid) is oxidized to A^- and A, and O_2 is reduced to O_2^- and HO_2^-, respectively. Once the oxygen has been used, a build up of Fe^{II}(tpps) is observed.

In order to find additional evidence for the redox cycling the reaction was repeated using an oxygen-sensitive electrode in order to follow the change in the oxygen concentration during the induction period. First the oxygen concentration of air-saturated water was measured and then a small volume of a concentrated ascorbate solution was added. Fig. 6 shows that after the addition of the ascorbate solution the oxygen concentration starts to decrease. After some time there is no longer any oxygen in the solution. This period during which the oxygen concentration is reduced to zero depends on the ascorbate concentration. If the same experiment is repeated in the presence of Fe^{III}(tpps) the decrease in the oxygen concentration is accelerated significantly (Fig. 7). The higher the Fe^{III}(tpps) concentration, the faster oxygen is used up at constant ascorbate concentration. This result therefore strongly supports the occurrence of a redox cycle during the induction period. The complex Fe^{III}(tpps) is reduced by ascorbate to Fe^{II}(tpps), which is again reoxidized by oxygen. During these reactions oxygen is consumed, and as soon as the oxygen is used up Fe^{II}(tpps) can be formed.

In the first redox cycle where Fe^{III}(tpps) is reduced by an excess of ascorbate in a nitrogen-saturated solution and then reoxidized by adding oxygen [Fig. 3(*a*); formation of the Fe^{II}-(tpps) and Fe^{III}(tpps) band] spectral changes could be observed. In the case of the second redox cycle no absorbance change can be seen (induction period), but there is indirect evidence of redox cycling from the measurements with the oxygen-sensitive electrode. Oxygen is consumed during the induction period, and as it becomes totally consumed Fe^{II}(tpps) is formed.

The results from these measurements clearly show that ascorbate reacts in a basic medium with oxygen, but that this reaction is catalysed by Fe^{III}(tpps). Therefore consumption of oxygen due to the reaction with ascorbate and due to the redox cycling of Fe(tpps) in (6) and (7) are responsible for the overall decrease in the oxygen concentration.

Conclusion

The results of this study have revealed conditions under which Fe^{III}(tpps) can be reduced to Fe^{II}(tpps) by ascorbate, or oxidized to $Fe^{III}(tpps^{\bullet+})$ accompanied by decomposition of tpps,

or undergo a redox cycle to Fe^{II}(tpps) and back to Fe^{III}(tpps). In a weakly acidic medium oxidation of the Fe^{III}(tpps) monomer to the Fe^{III}(tpps$^{\bullet+}$) radical cation and partial formation of Fe^{II}(tpps) could be observed, but there is no indication of a redox cycle. These observations are in agreement with our earlier results for sulfite ions,[20] indicating the ascorbic acid radicals interact in a similar way to the sulfite radicals.

In a basic medium ascorbate is able to reduce Fe^{III}(tpps) and a redox cycle can be performed by addition of oxygen, with immediate reoxidation of Fe^{II}(tpps) to Fe^{III}(tpps). The reduction of the Fe^{III}(tpps) dimer by ascorbate does not take place immediately. There is an induction period which depends on the oxygen concentration of the solution. The oxygen measurements showed a decrease in the oxygen concentration to nearly zero during the observed induction period. This decrease partially occurs because ascorbate reacts with oxygen in a basic medium. This reaction is however catalysed by the Fe^{III}(tpps) species. The oxygen measurements clearly showed that the oxygen consumption is much faster in the presence of Fe^{III}(tpps). A logical explanation is that in the presence of Fe^{III}(tpps) a redox cycle takes place which consumes oxygen and thus accelerates the decrease in the oxygen concentration. The catalytic effect of iron(III) ions has been observed before in an acidic medium,[25] although no evidence for a redox cycle was presented. The redox cycling and catalytic role of Fe^{III}(tpps) in a basic medium must be related to the higher lability of the μ-oxo dimer. The latter species will tend to undergo inner-sphere redox reactions with both ascorbate and oxygen due to the translabilization of the axial water molecules by the μ-oxo ligand. In this way we can account for the observed effects.

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References

1 A. P. Hong, D. W. Bahnemann and M. R. Hoffmann, *J. Phys. Chem.*, 1987, **91**, 6245.
2 B. Meunier, *Chem. Rev.*, 1992, **92**, 1411.
3 G. Behra and L. Sigg, *Nature* (*London*), 1990, **344**, 419.
4 M. W. Grinstaff, M. G. Hill, J. A. Labinger and H. B. Gray, *Science*, 1994, **264**, 1311.
5 S. M. Chen, *J. Electroanal. Chem.*, *Interfacial Electrochem.*, 1996, **407**, 123.
6 W. Nam, H. J. Kim, S. H. Kim, R. Y. N. Ho and J. S. Valentine, *Inorg. Chem.*, 1996, **35**, 1045.
7 A. Maldotti, C. Bartocci, G. Varari, A. Molinari, P. Battioni and D. Mansuy, *Inorg. Chem.*, 1996, **35**, 1126.
8 J. G. Muller, R. P. Hickerson, R. J. Perez and C. J. Burrows, *J. Am. Chem. Soc.*, 1997, **119**, 1501.
9 J. T. Groves, J. Lee and S. S. Marla, *J. Am. Chem. Soc.*, 1997, **119**, 6269 and refs. therein.
10 A. Bakac and W.-D. Wang, *J. Am. Chem. Soc.*, 1996, **118**, 10 325 and refs. therein.
11 C. Brandt and R. van Eldik, *Chem. Rev.*, 1995, **95**, 119 and refs. therein.
12 C. Brandt, I. Fabian and R. van Eldik, *Inorg. Chem.*, 1994, **33**, 687.
13 V. Zang and R. van Eldik, *Inorg. Chem.*, 1990, **29**, 4462.
14 F. F. Prinsloo, J. J. Pienaar, R. van Eldik and H. Gutberlet, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2373.
15 F. F. Prinsloo, J. J. Pienaar and R. van Eldik, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 293.
16 V. Lepentsiotis, F. F. Prinsloo, R. van Eldik and H. Gutberlet, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2135.
17 F. F. Prinsloo, J. J. Pienaar and R. van Eldik, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4393.
18 F. F. Prinsloo, J. J. Pienaar and R. van Eldik, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1871.
19 M. A. Kline, M. H. Barley and T. J. Meyer, *Inorg. Chem.*, 1987, **26**, 2196.
20 V. Lepentsiotis, R. van Eldik, F. F. Prinsloo and J. J. Pienaar, unpublished work.
21 B. Bänsch, P. Martinez, D. Uribe, J. Zuluaga and R. van Eldik, *Inorg. Chem.*, 1991, **30**, 4555.
22 B. Bänsch, P. Martinez, J. Zuluaga, D. Uribe and R. van Eldik, *Z. Phys. Chem.*, 1991, **170**, 59.
23 F. L. Harris and D. L. Toppen, *Inorg. Chem.*, 1978, **17**, 74.
24 G. A. Tondreau and R. G. Wilkins, *Inorg. Chem.*, 1986, **25**, 2745.
25 M. M. Taqui Khan and A. E. Martell, *J. Am. Chem. Soc.*, 1967, **89**, 4176.
26 E. B. Fleischer, J. M. Palmer, T. S. Srivastava and A. Chatterjee, *J. Am. Chem. Soc.*, 1971, **93**, 3162.
27 C. Brandt, N. Coichev, E. Hostert and R. van Eldik, *GIT Fachz. Lab.*, 1993, **37**, 277.
28 J. Salbeck, *Anal. Chem.*, 1993, **65**, 2169.
29 M. H. Barley, K. J. Takeuchi and T. J. Meyer, *J. Am. Chem. Soc.*, 1986, **108**, 5876.
30 E. K. Barefield and M. T. Mocella, *J. Am. Chem. Soc.*, 1975, **97**, 4238.
31 J. Vasilevskis, D. C. Olson and K. Loos, *Chem. Commun.*, 1970, 1718.

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