Electron Spin Resonance Study of the Species formed by Reduction of Iron(III) Chelates of Tetrasodium 3,10,17,24-Tetrasulphonatophthalocyanine in Aqueous Solution

By **Thomas D. Smith,* Cheng H. Tan,** and **David J. Cookson,** Chemistry Department, Monash University, Clayton, Victoria, Australia 3168
John R. Pilbrow, Physics Department, Monash University, Clayton, Victoria, Australia 3168

Electron spin resonance measurements show that the deep blue iron(III) chelate of 3,10,17,24-tetrasulphonatophthalocyanine (tspc) exists as a low-spin iron(III) species in aqueous solutions of low pH and containing 20% v/v of dimethylformamide (dmf). Reduction of iron(III) tspc with sodium tetrahydroborate in aqueous solution leads to the formation of the e.s.r.-detectable violet coloured iron(I) tspc whose chemical stability at room temperature is increased in aqueous solutions containing 20% v/v dmf. Reduction of iron tspc with $Na[BH_4]$ in aqueous solutions containing pyridine leads to the formation of a violet coloured species which does not exhibit an e.s.r. spectrum and is thought to be an iron(I) radical anion tspc chelate. This species is oxidised cleanly to iron(III) tspc by molecular oxygen. Reaction of iron(III) tspc with hydroxylamine under carefully controlled conditions of pH leads to the formation of a nitrosyl complex of the iron tspc chelate.

A PREVIOUS study using e.s.r. spectroscopy to identify the products formed by reduction of the manganese chelates of tetrasodium 3,10,17,24-tetrasulphonatophthalocyanine, Na_4(tspc), on addition of various reducing agents, showed that $[Mn^0(tspc)]^{6-}$ is formed by reduction with hydrazine, sodium sulphide, or dithionite whereas other reduction products are formed on the addition of sodium tetrahydroborate under various circumstances.[1] The present investigation was carried out to identify the reduction products formed by iron(III) tspc when treated with similar reagents.

RESULTS

Aqueous solutions of iron tspc (5.0×10^{-3} mol dm^{-3}) do not exhibit an e.s.r. spectrum at room temperature or in frozen solution (133 K) over the pH range 2.0—9.0. The addition of dimethylformamide (dmf) to an acidic (pH *ca.* 2.3) aqueous solution of the iron(III) chelate makes possible the observation of the e.s.r. spectrum shown in Figure 1 at sample temperatures of 133 K. This spectrum is attributed to a low-spin form of iron(III) tspc and consideration of a spin Hamiltonian of the form $\mathcal{H} = \beta \sum_{i=x,y,z} g_i S_i B_i$ leads to the following magnetic parameters: $g_x = 1.830$, $g_y = 2.250$, and $g_z = 2.575$ obtained by computer simulation of the e.s.r. spectrum. At higher pH the intensity of this signal is diminished such that at pH 5.5 it is no longer observable.

Reductions with Sodium Tetrahydroborate.—An immediate colour change from blue to violet occurs after addition of an aqueous solution of $Na[BH_4]$ to an aqueous solution of iron(III) tspc. The changes in the u.v.–visible absorption spectra of the chelate species which result from this reduction process and others to be described are shown in Figure 2. The e.s.r. spectrum of the reduction product is shown in Figure 3 and is attributed to a low-spin iron(I) chelate. Measurements of the areas under the curve made on the e.s.r. spectra due to the low-spin iron(III) tspc and iron(I) tspc showed that the spin densities were closely similar and pointed to the complete conversion of iron(III) tspc to iron(I) tspc under the reducing conditions used. Computer simulation of the e.s.r. spectrum due to the low-spin iron(I) tspc species is achieved using the values $g_{\parallel} = 2.015$ and $g_{\perp} = 2.33$.

On standing under nitrogen the violet colour faded to give a brown product undoubtedly due to decomposition of the phthalocyanine. The presence of 20% v/v dmf increased the stability of the iron(I) tspc such that the intensity of the signals shown in Figure 3 decreased by one half of that observed in fresh solutions after *ca.* 3 h standing at room temperature. The addition of $Na[BH_4]$ to an acidic

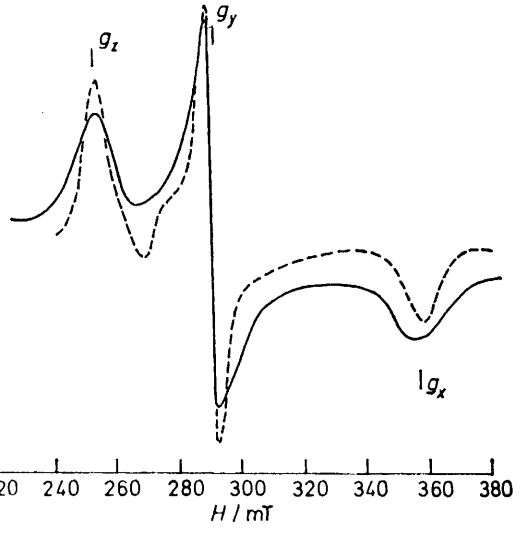


FIGURE 1 E.s.r. spectrum of a frozen aqueous solution (133 K) containing iron(III) tspc (5.0×10^{-3} mol dm^{-3}) at pH 2.30 and 20% v/v dmf. Microwave frequency 9 149 MHz. The broken line represents the computed lineshape using the magnetic parameters: $g_x = 1.830$; $g_y = 2.25$; and $g_z = 2.575$

solution (pH *ca.* 2.5) where the predominant species in solution prior to the addition of reducing agent is the e.s.r.-detectable low-spin iron(III) tspc ($g_1 = 1.83$; $g_2 = 2.25$; $g_3 = 2.57$) again gives rise to a violet solution, the e.s.r. spectra of which is the same as that observed in neutral solution and shown in Figure 3. Addition, under nitrogen, of the reducing agents such as sodium dithionite, sodium sulphide, or potassium ferrocyanide to acid solutions (pH *ca.* 2.5) of iron(III) tspc containing 20% v/v dmf results in the immediate formation of a green solution and complete disappearance of the e.s.r. signal due to the low-spin iron(III)

tspc species present initially, a result entirely consistent with the formation of iron(II) tspc. Again, the addition of $Na[BH_4]$ to an aqueous solution of iron(III) tspc containing 20% v/v of pyridine gives rise to green solutions which on

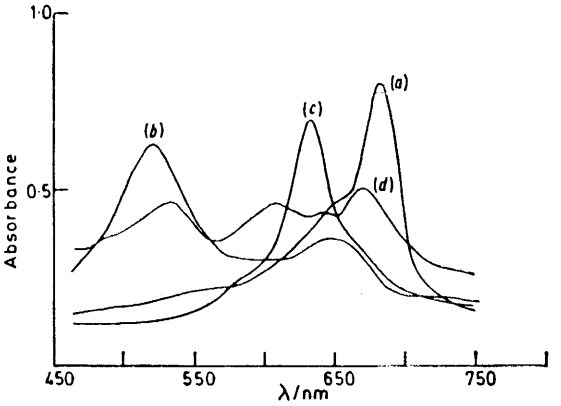


FIGURE 2 U.v.–visible absorption spectra for aqueous solutions containing iron(III) tspc (1.50×10^{-5} mol dm^{-3}) and (*a*) 20% v/v dmf, (*b*) $Na[BH_4]$ (1.50×10^{-3} mol dm^{-3}) and 20% v/v dmf, (*c*) 20% v/v pyridine, (*d*) $Na[BH_4]$ (1.50×10^{-3} mol dm^{-3}) and 20% v/v pyridine. 1-cm Glass cells

standing for some 10 min turn violet. Surprisingly, the violet solution does not exhibit an e.s.r. spectrum in the frozen state. Exposure of the violet solution to air gave rise initially to a greenish blue solution which ultimately regenerated the blue solution due to iron(III) tspc.

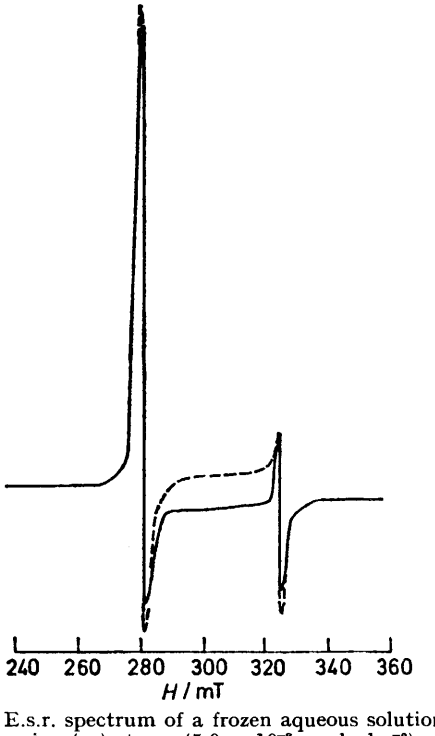


FIGURE 3 E.s.r. spectrum of a frozen aqueous solution (133 K) containing iron(III) tspc (5.0×10^{-3} mol dm^{-3}) to which $Na[BH_4]$ has been added. Microwave frequency 9 149 MHz. The broken line represents the computed lineshape using the magnetic parameters: $g_{\parallel} = 2.015$ and $g_{\perp} = 2.33$

Reductions with Hydroxylamine.—The reaction of iron(III) tspc (5.0×10^{-3} mol dm^{-3}) with a 10 mol excess of hydroxylamine in 20% v/v dmf–aqueous solution at pH 5.0 and under nitrogen results in an immediate colour change from blue to green. When a 100-fold mol excess of hydroxylamine is added under nitrogen to an aqueous solution of iron(III) tspc in 20% dmf–water such that the pH of the final solution was *ca.* 5.0, again the solution turns a green colour immediately on mixing the reagents. However, in these circumstances the green colour persists for a few minutes before the blue colour of the solution is established.

The e.s.r. spectrum of a sample at 133 K of a 20% v/v dmf–aqueous solution of iron(III) tspc (5.0×10^{-3} mol dm^{-3}) containing a 10 mol excess of hydroxylamine at pH 5.0 is shown in Figure 4. A similar spectrum is obtained by rapid freezing of the green solution formed in a dmf–aqueous solution containing iron(III) tspc and a 100-fold mol excess of hydroxylamine. The e.s.r. spectrum of the same solution, but blue in colour as a result of standing a few minutes,

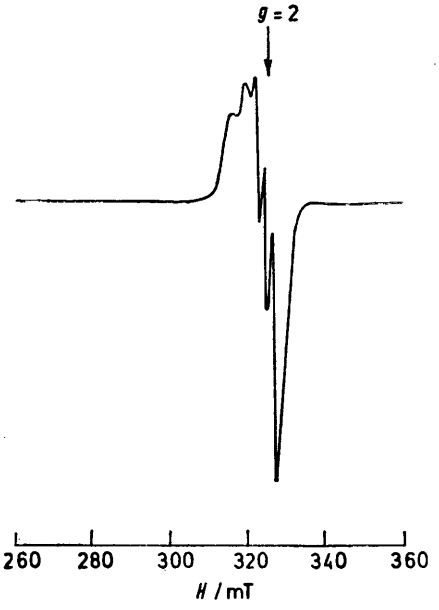


FIGURE 4 E.s.r. spectrum of a frozen aqueous solution (133 K) containing iron(III) tspc (5.0×10^{-3} mol dm^{-3}), hydroxylamine hydrochloride (5.0×10^{-2} mol dm^{-3}), and 20% v/v dmf at pH 5.0. Microwave frequency 9 149 MHz

was of the same intensity, though the fine structure of the peaks shown in Figure 4 had become less resolved.

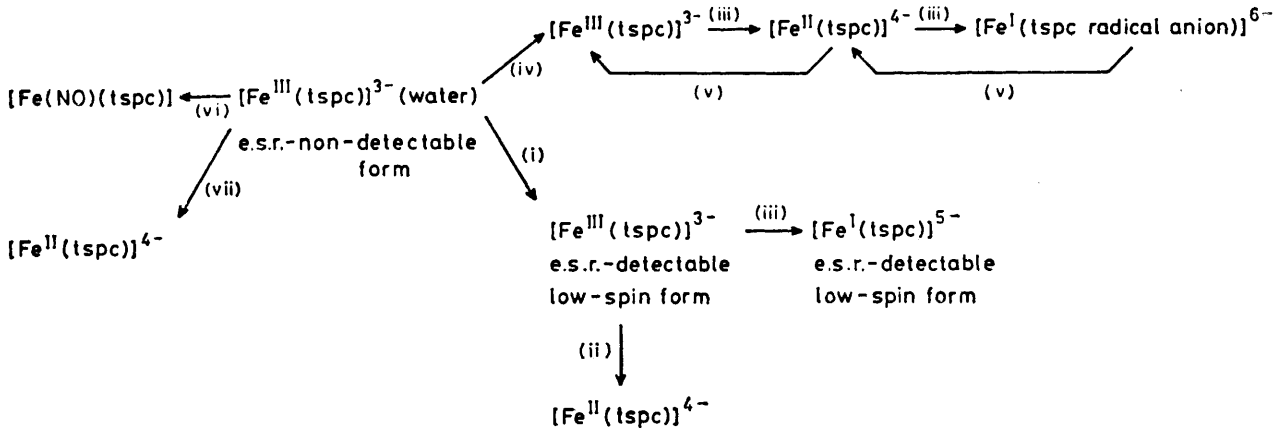
The addition under nitrogen of hydroxylamine to 20% v/v dmf–aqueous solutions containing iron(III) tspc such that the final pH of the solution is 7.0 or 10.0 results in a colour change from blue to green. However, no new e.s.r. signals are observed for samples of these solutions at reduced temperatures, and it is concluded that in these circumstances reduction to iron(II) tspc occurs.

DISCUSSION

The various chemical changes brought about by addition of reducing agents to largely aqueous solutions of iron(III) tspc are summarised in the Scheme.

Reduction of iron(III) tspc by sodium tetrahydroborate in aqueous solution under various circumstances leads to the formation of iron(I) tspc, characterised by the magnetic parameters $g_{\parallel} = 2.015$ and $g_{\perp} = 2.33$ which are close to those found for the iron(I) tetraphenylporphyrin ($g_{\parallel} = 1.93$; $g_{\perp} = 2.30$) which is thought to be a four-

co-ordinate species.[2] The magnetic parameters for the iron(I) phthalocyanine chelate in dimethyl sulphoxide are $g_{\parallel} = 1.961$ and $g_{\perp}$ 2.077 where the iron is five-co-ordinate.[3] The iron tspc species formed by the tetrahydroborate reduction in aqueous solutions containing 20% v/v of pyridine, violet in colour but not exhibiting an e.s.r. spectrum in frozen solution, is possibly the even-electron species involving iron(I) and an anion radical of the tspc, as observed previously in reductions of iron(II) phthalocyanine.[3] It is of interest that this addition of dmf enables measurements of the e.s.r. spectra due to the iron(III) tspc to be made at least at low pH. This procedure, while allowing ample time for measurements to be made, suffers the disadvantage of reducing the chemical stability of iron(III) tspc, the decomposition of which in aqueous solutions is marked by gradual change of colour from deep blue to green and the appearance of various e.s.r.-detectable low-spin iron(III) species, separable by paper chromatography, when the solutions are allowed to stand at room temperature for a matter of days. The decomposition can be accelerated by heating the solutions.



SCHEME (i) 20% v/v dmf, pH 2.0, (ii) $Fe(CN)_6^{4-}$, $S_2O_4^{2-}$, S^{2-}, (iii) BH_4^-, (iv) 20% v/v pyridine, (v) O_2, (vi) NH_2OH, pH 5.05, (vii) NH_2OH, pH 7.0

system allows a clean oxidation by molecular oxygen to form iron(II) tspc and ultimately iron(III) tspc.

The e.s.r. spectrum of the product formed by reaction of an aqueous solution containing iron(III) tspc and hydroxylamine at pH 5.0 is closely similar to that of the six-co-ordinate nitric oxide complex of iron(II) tetraphenylporphyrin–piperidine complex,[4] various nitrosyl–heme complexes,[5] nitrosyl–hemoglobin,[6–10] and nitrosyl–myoglobin complexes.[11] The various studies on these systems have shown that the odd electron which originates on nitric oxide is highly delocalised to the iron atom in the complex.[12] Mössbauer spectroscopic measurements show a substantial spin transfer in nitrosyl–hemoglobin to the iron orbital which approaches an iron(I) type electronic configuration,[13] while e.s.r. studies have led to the conclusion that the deviation of the g tensor from the electron g values is an indication that the unpaired electron is in one of the antibonding e_g orbitals of iron.[5,6]

EXPERIMENTAL

The iron(III) chelate of 3,10,17,24-tetrasulphonatophthalocyanine was prepared by the method outlined by Weber and Busch.[14] The product was recrystallised several times and separated from accompanying impurities by column chromatography using Sephadex G10.[15] The

In the experiments involving the addition of various reducing agents the original mixing of solutions and subsequent transfer operations were carried out under a nitrogen atmosphere. The e.s.r. measurements, at room temperature and of frozen solutions, were made on a Varian E12 spectrometer at a microwave frequency of 9 149 MHz.

[9/1471 *Received*, 17*th September*, 1979]

REFERENCES

[1] D. J. Cookson, T. D. Smith, J. F. Boas, P. R. Hicks, and J. R. Pilbrow, *J.C.S. Dalton*, 1977, 211.
[2] I. A. Cohen, D. Ostfeld, and B. Lichtenstein, *J. Amer. Chem. Soc.*, 1972, **94**, 4522.
[3] A. B. P. Lever and J. P. Wilshire, *Inorg. Chem.*, 1978, **17**, 1145.
[4] B. B. Wayland and L. W. Olson, *J. Amer. Chem. Soc.*, 1974, **96**, 6037.
[5] H. Kon and N. Katoaka, *Biochemistry*, 1969, **8**, 4757.
[6] J. Kon, *J. Biol. Chem.*, 1968, **243**, 4350.
[7] J. C. W. Chien, *J. Chem. Phys.*, 1969, **51**, 4220.
[8] H. Kon, *Biochem. Biophys. Acta*, 1975, **379**, 103.
[9] H. Rein, O. Ristau, and W. Scheler, *FEBS Letters*, 1972, **24**, 24.
[10] A. Szabo and M. F. Perutz, *Biochemistry*, 1976, **15**, 4427.
[11] L. C. Dickenson, *J. Amer. Chem. Soc.*, 1971, **93**, 5036.
[12] T. Yonetani, H. Yamamoto, J. E. Cowan, J. S. Leigh, and G. H. Reed, *J. Biol. Chem.*, 1972, **247**, 2447.
[13] G. Lang and W. Marshall, *J. Mol. Biol.*, 1966, **18**, 385.
[14] J. H. Weber and D. H. Busch, *Inorg. Chem.*,1965, **4**, 469.
[15] G. McLendon and A. E. Martell, *Inorg. Chem.*, 1977, **16**, 1812.