

## Photoejection of Dioxygen from Cobalt Porphyrin ( $\eta^1$ -Azaferrocene)( $\eta^1$ -O<sub>2</sub>) Complexes

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The visible light irradiation of cobalt porphyrin ( $\eta^1$ -azaferrocene)( $\eta^1$ -O<sub>2</sub>) complexes in toluene at 180–200 K results in the photoejection of triplet oxygen, whereas under the same conditions their  $\eta^1$ -pyridine counterparts are photostable.

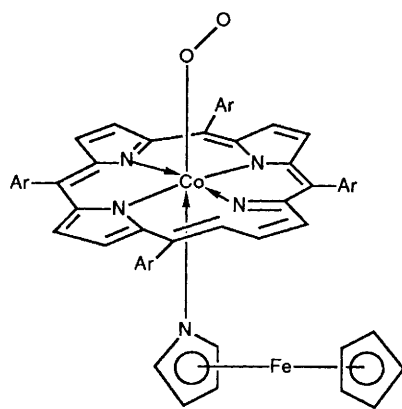
There is continuing interest in the reversible complexation of dioxygen by cobalt(II) chelates [e.g., cobalt(II) porphyrins, CoP] and in the chemistry of resulting dioxygen complexes.<sup>1–4</sup> It has been found that although CoP themselves are poor oxygen binders, their corresponding monobase adducts CoP(B) (B denotes a Lewis base, usually pyridine or imidazole) formed reversibly in solution readily bind dioxygen to form CoP(B)( $\eta^1$ -O<sub>2</sub>).

In connection with our studies on the co-ordinating properties of azaferrocene, ( $\eta^5$ -C<sub>4</sub>H<sub>4</sub>N)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe,<sup>5</sup> we have recently<sup>6</sup> reported that this organometallic base also forms adducts of the type CoP( $\eta^1$ -azaferrocene) and CoP( $\eta^1$ -azaferrocene)( $\eta^1$ -O<sub>2</sub>) (**1**).

Rather surprisingly we have found that the thermodynamics of dioxygen binding by Co(tpp)( $\eta^1$ -azaferrocene)<sup>6</sup> (tpp = tetra-*p*-tolylporphyrin) are practically the same as those of its  $\eta^1$ -pyridine counterpart, Co(tpp)(py). We thought, however, that different behaviour of the excited states of the corre-

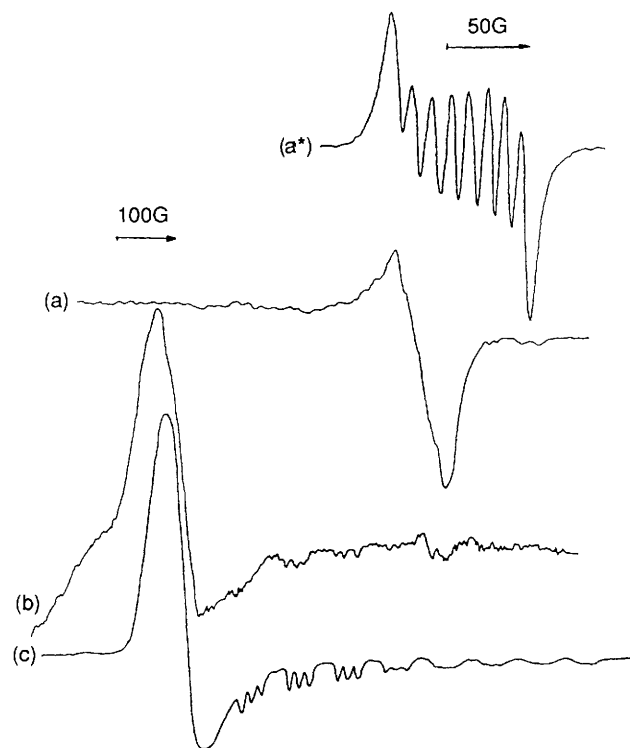
sponding  $\eta^1$ -dioxygen adducts could be expected since in the former a photoinduced electron or energy transfer may occur between two metal centres.

Here we report that the photochemical behaviour of (**1**) differs markedly from that of CoP(py)( $\eta^1$ -O<sub>2</sub>). We have



(1)

- a; Ar = Ph  
b; Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>  
c; Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>



**Figure 1.** Typical ESR spectra: (a) (**1a**) in aerated toluene glass ( $10^{-3}$  M) at 100 K; (a\*) the hyperfine structure of the signal of (**1a**) observed in fluid solution at 200 K ( $g_{\text{iso}}$  2.016,  $a^{\text{Co}}$  11.3 G); (b) the sample (a) after photolysis at 180 K and refreezing to 100 K; (c) Co(tpp)( $\eta^1$ -azaferrocene) formed by irradiation of (**1a**) in partly degassed solution at 100 K ( $g_{\perp}$  2.321,  $g_{\parallel}$  2.021;  $a^{\text{Co}}$  83.0 G,  $a^{\text{N}}$  17.2 G).

**Table 1.** First-order rate constants for decomplexation of O<sub>2</sub> from (1) (10<sup>-3</sup> mol dm<sup>-3</sup>) under visible light irradiation<sup>a</sup> at 180 K.

Complex	<i>k</i> /s <sup>-1</sup>
(1a)	4.3 × 10 <sup>-2</sup>
(1b)	3.1 × 10 <sup>-3</sup>
(1c)	1.2 × 10 <sup>-3</sup>

<sup>a</sup> 900 W Xe lamp with CS-051 filter.

found, using ESR spectroscopy, that visible light irradiation brings about the dissociation of dioxygen from (1) whereas the complexes CoP(py)(η<sup>1</sup>-O<sub>2</sub>) proved photostable. This constitutes, to our knowledge, the first example of the photodissociation of O<sub>2</sub> from a six-co-ordinated (η<sup>1</sup>-O<sub>2</sub>)(η<sup>1</sup>-amine) complex of CoP in solution.

The ESR spectra show that in a solution of the corresponding CoP (10<sup>-3</sup> mol dm<sup>-3</sup>) and azaferrocene (10<sup>-3</sup> mol dm<sup>-3</sup>) in aerated toluene at 100–200 K there is complete formation of (1a–c). A typical spectrum, centred at *g* ~ 2, is presented in Figure 1(a) and the spectral parameters are practically the same as those of corresponding pyridine adducts.<sup>1</sup> The visible light irradiation of such a solution (900 W Xenon Lamp and CS 051 filter) results in the decay of (1) with formation of the corresponding CoP(η<sup>1</sup>-azaferrocene) complexes, whose ESR spectra were observed when the samples were frozen at 100 K. As shown in Figure 1(b) the hyperfine structure is partly visible.

Well resolved spectra, Figure 1(c), were obtained when the solutions were partly degassed by a brief purge with argon. The ESR spectra of such samples displayed signals of both (1) and the corresponding CoP(η<sup>1</sup>-azaferrocene) complexes; on irradiation the former disappeared and the latter increased in intensity. This behaviour was fully reversible. When the irradiation was stopped the reverse process, complexation of dioxygen by CoP(η<sup>1</sup>-azaferrocene), was observed.

Further experiments provided deeper insight into this process. Firstly, we have found that irradiation of either the Soret (~410 nm) of the visible band (~540 nm) of (1) is photoactive. Secondly, the decay of (1) obeyed first-order kinetics. Electron donating substituents in the *para* position of the phenyl rings cause a decrease in the rate constant (Table 1), since they increase the electron density at cobalt which stabilises η<sup>1</sup>-dioxygen complexes. Thirdly, we have not observed, by the spin trapping technique, the formation of either free superoxide (O<sub>2</sub><sup>-•</sup>) or singlet dioxygen in photolysed solutions. Considering all these facts, we conclude that photolysis of (1) results in the homolytic rupture of the

cobalt–oxygen bond to give CoP(η<sup>1</sup>-azaferrocene) and triplet oxygen. In contrast, we have not observed the photodissociation of O<sub>2</sub> from pyridine-based analogues of (1), *i.e.*, CoP(py)(η<sup>1</sup>-O<sub>2</sub>), under these conditions.

It is noteworthy that some examples of photo-ejection of dioxygen from weaker oxygen binders, (η<sup>1</sup>-dioxygen) complexes of CoP without an axial base, have already been reported.<sup>7,8</sup> Hoshino<sup>7</sup> has observed such a process when an aerated solution of Co(tpp) in methyltetrahydrofuran was irradiated with visible light at low temperatures. More recently, both photo-complexation and photo-decomplexation of <sup>3</sup>O<sub>2</sub> were observed for a series of CoP in aqueous micellar solutions and microemulsions.<sup>8</sup>

The observed photolability of dioxygen in (1) could be explained if one assumes that in the photoexcited state an electron transfer from cobalt to iron takes place. Such transfer, diminishing the electron density at the cobalt centre, would markedly weaken the cobalt–oxygen bond and favour decomplexation of O<sub>2</sub>. After decomplexation of O<sub>2</sub>, the reverse electron transfer (Co ← Fe) would lead back to CoP(η<sup>1</sup>-azaferrocene). However, a rapid photodissociation of azaferrocene from (1) followed by the thermal loss of O<sub>2</sub> from the resulting five-co-ordinated complex CoP(O<sub>2</sub>) and recomplexation of azaferrocene could not be excluded.

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## References

- 1 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.
- 2 J. P. Collman, T. R. Halbert, and K. S. Suslick, in 'Metal Ion Activation of Dioxygen,' ed. T. S. Spiro, p. 6.
- 3 E. C. Niederhoffer, J. H. Timmons, and A. E. Martell, *Chem. Rev.*, 1984, **84**, 137.
- 4 H. R. Mäcke and A. F. Williams, in 'Photo-induced Electron Transfer,' eds. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, ch. 5.2.
- 5 For recent work on the co-ordination chemistry of 2,3,4,5-tetramethylazaferrocene and octamethyl-1,1'-diazaferrocene see: N. Kuhn, M. Schulten, E. Zauder, N. Augart, and R. Boese, *Chem. Ber.*, 1989, **122**, 1891; N. Kuhn, E.-M. Horn, R. Boese, and D. Bläser, *ibid.*, 1989, **122**, 2275.
- 6 J. Zakrzewski and C. Giannotti, *J. Organomet. Chem.*, 1990, **385**, C23–C26.
- 7 M. Hoshino, *Chem. Phys. Lett.*, 1985, **120**, 50.
- 8 D. A. Lerner, M. Barcelo Quintal, P. Maillard, and C. Giannotti, *J. Chem. Soc., Perkin Trans. 2*, in the press.