

environmentally sensitive luminescence emissions under high resolution suggest themselves.

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- (23) In general, radiationless deexcitation via coordinated R-OH, R-SH, or R-NH₂ moieties must also be considered; however, these are absent in the systems under study here. A term: $k_{D_2O}(1 - \chi_{H_2O})$ might also be included for completeness; however, it has been shown^{14,19} that $k_{D_2O}/k_{H_2O} \leq 0.01$, so it can be safely excluded.
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William DeW. Horrocks, Jr.,* Gregory F. Schmidt
Daniel R. Sudnick, Carter Kittrell, Robert A. Bernheim

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

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Substituent Effects on the Formation Constants of Iron(III) and Iron(II) Tetraphenylporphyrin-Pyridine Complexes

Sir:

In recent years there has been considerable interest in linear free energy relationships involving metalloporphyrins. These have focused on the effect of porphyrin ring basicity in determining polarographic half-wave potentials,¹⁻⁴ electron transfer kinetics,⁵ spectroscopic properties,⁶ and stability constants for axial ligand addition to form 1:1 and 2:1 complexes.^{3,7-11}

Recent publications have shown that the presence of electron withdrawing groups on a porphyrin ring contribute to substantially increased stability constants for Lewis base complexation of cobalt(II),^{3,9} nickel(II),^{8,10} vanadyl(II),¹⁰ and zinc(II)¹¹ para and meta substituted tetraphenylporphyrins. The magnitude of interaction of the central metal with the porphyrin ring was measured using the Hammett linear free energy relationship.¹²

$$\log \frac{K^x}{K^H} = \Sigma \sigma \rho \quad (1)$$

In all previous studies of +2 metals ρ was positive and found to increase in the order VO(*p*-X)TPP (0.113) < Co(*p*-X)TPP (0.166) < Zn(*p*- or *m*-X)TPP (0.188) << Ni(*p*-X)TPP (0.331) < Ni(*m*-X)TPP (0.413). Of the metals investigated only Ni(*p*-X)TPP and Ni(*m*-X)TPP formed 2:1 adducts, and it was therefore suggested that ρ might be dependent on the number of axial ligands.³ Another suggested possibility was that ρ increased with the number of metal d electrons.¹⁰ However, the differences in ρ are small for the monoligated complexes containing vanadyl, cobalt, and zinc and one might be tempted to argue that within experimental error, no significant differences exist in the extent of metal, porphyrin ring interaction.

Recently, Walker et al.¹³ have reported linear free energy relationships for the addition of Lewis bases to Fe(*p*-X)TPPCl to form 1:1 and 2:1 complexes. For Fe(*p*-X)TPP·B₂Cl, where B = *N*-methylimidazole, plots of $\log K^X/K^H$ vs. 4σ gave a negative slope of $\rho = -0.39$ in CHCl₃ compared to a positive slope for all of the previously investigated +2 metals. The change in sign of the reaction constant was rationalized on the basis of a stabilization of the positively charged Fe(III) and there appeared to be a clear indication that stabilization of an ion paired product, FeTPP·B₂⁺Cl⁻, predominated the reactions of Fe(*p*-X)TPPCl with axial ligands. However, a comparison of substituent effects with Fe^{II}(*p*-X)TPP·B₂ was not presented so that suggestions of charge stabilization could only be made based on comparisons with equilibrium constants for Ni^{II}(*p*-X)TPP·B₂. Furthermore, no conclusions could be drawn from stability constants of Fe(*p*-X)TPP·BCl presumably due to the small values of the equilibrium constant and scatter in the data.

In this communication we present the first comparison between substituent effects on Fe^{II}P·B₂, Fe^{III}P·B₂Cl, and Fe^{III}P·BCl in DMF where B is pyridine and P represents (*p*-X)TPP or (*m*-X)TPP. Both iron(III) and iron(II) porphyrins are known to form bis coordination complexes with pyridine^{14,15} while iron(III) will also form a monoligand adduct in some solvents.¹³ At a platinum electrode reversible reductions are observed for both Fe(III) and Fe(II) in DMF.¹⁶ Stability constants for Fe^{II}P·BCl, Fe^{III}P·B₂Cl, and Fe^{II}P·B₂ can then be evaluated from shifts in polarographic peak potentials between the uncomplexed porphyrin in neat DMF and the complexed species in DMF-pyridine mixtures.¹⁷

A typical cyclic voltammogram of Fe(*p*-CH₃)TPPCl in neat DMF, 11.5 mM and 1.58 M pyridine-DMF mixtures is shown in Figure 1. On adding pyridine, peak potentials for Fe^{III}P·Cl reduction to Fe^{II}P (peak 1) shifted only slightly, while peak potentials for reoxidation of Fe^{II}P (peak 2) shifted anodically by over 300 mV with increasing pyridine concentration. At the same time, a new peak (identified as peak 3, Figure 1) appeared which was separated by 60 mV from peak 2 and also shifted significantly with changes in the pyridine concentration.

Using the magnitude of the potential shifts Scheme I may be formulated. Assignments of DMF as an axial ligand are based on analogous assignments in Me₂SO and DMA where up to two ligands are coordinated to iron(II) and iron(III).¹⁵

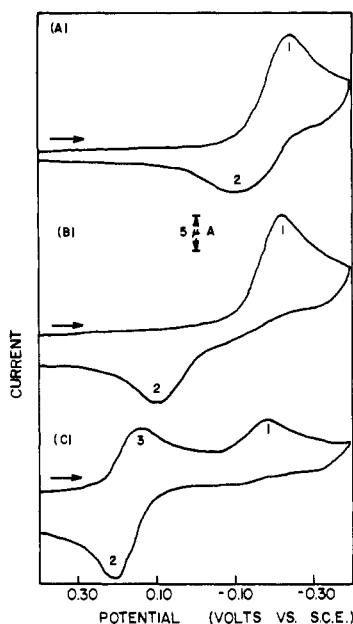
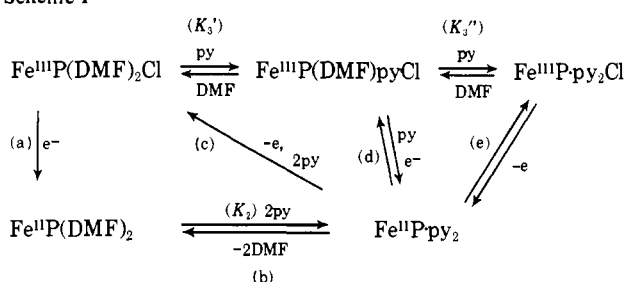


Figure 1. Cyclic voltammogram of 0.941 mM Fe(*p*-CH₃)TPPcI at a platinum electrode in DMF-pyridine mixtures 0.1 M TBAP: (a) neat DMF; (b) 11.5 mM pyridine, and (c) 1.58 M pyridine. Scan rate = 100 mV/s.

Scheme I



At pyridine concentrations between 10^{-3} and 10^{-2} M FeTPPcI is not complexed by pyridine¹⁴ and the reduction-oxidation sequence is via (a), (b), (c). This is shown in Figure 1B. From pyridine concentrations of 10^{-2} to 5×10^{-1} M the unbound iron(III) complex still exists in solution and reduction to yield Fe^{II}TPPpy₂ is via path (a), (b) (peak 1). Reoxidation, however, is via path (d) in all cases so that the second sweep consists of two reduction peaks and one oxidation peak. Only at concentrations above 1 M pyridine will the bispyridine-iron(III) complex be observed and under these conditions the overall reversible reaction will proceed simultaneously via path (e) (peaks 3 and 2) and paths (a), (b), (e) (peaks 1 and 2). This is shown in Figure 1C where two reduction peaks and only a single oxidation peak are observed. (Under these conditions the presence of unbound Fe^{III}TPP(DMF)₂Cl reflects a kinetic rather than a thermodynamic situation since all of the iron(III) is converted to Fe^{III}TPPpy₂Cl after initial complexation.)

In the above scheme the notation K_2 is utilized to represent the overall stability constant for addition of two pyridine molecules to Fe^{II}P(DMF)₂. Stepwise stability constants for single pyridine addition to Fe^{III}P(DMF)₂Cl are given the notation K_3' and K_3'' , and the overall stability constant $K_3 = K_3'K_3''$. This scheme is not novel and has been suggested in part by several other laboratories.^{14,15} Polarographic wave analysis showed no evidence for complexation of iron(I) in DMF, confirming previous studies at the DME.¹⁶

Plots of $\log K^X/K^H$ vs. 4σ are shown in Figure 2. In agreement with the $\rho = -0.39$ obtained by Walker et al.¹³ for

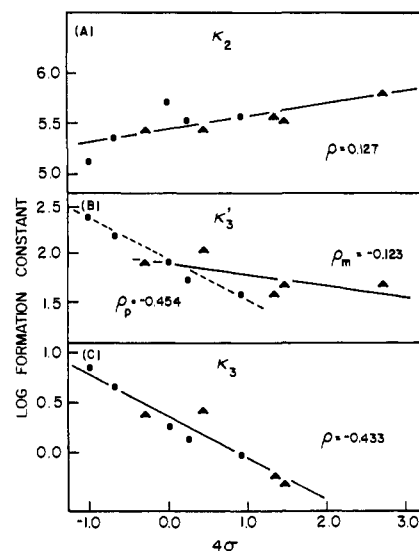


Figure 2. Plot of $\log K^X/K^H$ vs. 4σ for pyridine binding to iron(II) and iron(III) para and meta substituted tetraphenylporphyrin in DMF, 0.1 M TBAP: (a) Fe(*p*- or *m*-X)TPPpy₂, (b) Fe(*p*- or *m*-X)TPP(DMF)pyCl, and (c) Fe(*p*- or *m*-X)TPPpy₂Cl. Para substituted complexes are represented by ● and meta substituted complexes by ▲.

Fe^{II}P·B₂Cl formation in chloroform, we obtained a $\rho = -0.433$ in DMF. The reaction constant was also negative for formation of the monopyridine adduct, Fe^{III}PpyCl, and in this case gave distinct values for compounds containing para and meta substituents. Compounds containing para substituents gave a $\rho_p = -0.454$ while those containing meta substituents gave a reduced $\rho_m = -0.123$. As might be predicted, a positive $\rho = 0.127$ was calculated for Fe(*p*- or *m*-X)Ppy₂ formation.

When considering the uncertainty in the measurement of ρ , it appears that there is no substantial difference in substituent effects between VO(*p*-X)TPP, Fe(*p*- or *m*-X)TPP, Co(*p*-X)TPP, or Zn(*p*- or *m*-X)TPP and that Ni(*p*- or *m*-X)TPP is an exception in that a larger degree of interaction is observed for this compound. It has been previously observed that the magnitude of ρ increases with the number of axially coordinated ligands.^{3,10} However, since both Ni(*p*- or *m*-X)TPP and Fe(*p*- or *m*-X)TPP form 2:1 complexes, it appears that the degree of axial ligand binding does not influence ρ for +2 metalloporphyrins. This is not clear, however, for +3 metalloporphyrins where two distinct relationships are observed for Fe(*p*-X)TPP(DMF)B ($\rho = -0.454$) and Fe(*m*-X)TPP(DMF)B ($\rho = -0.123$) but only a single relationship ($\rho = -0.433$) for Fe(*p*- or *m*-X)TPP·B₂Cl.

We are currently investigating the effect of substituents on mono- and bis-ligand adducts of other +3 and +4 metalloporphyrins which, we hope, will provide an unambiguous conclusion as to the competing effects of metal charge state, number of axially coordinated ligands, and porphyrin ring basicity in predicting metalloporphyrins stability constants.

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K. M. Kadish,* L. A. Bottomley

Department of Chemistry, University of Houston
Houston, Texas 77004

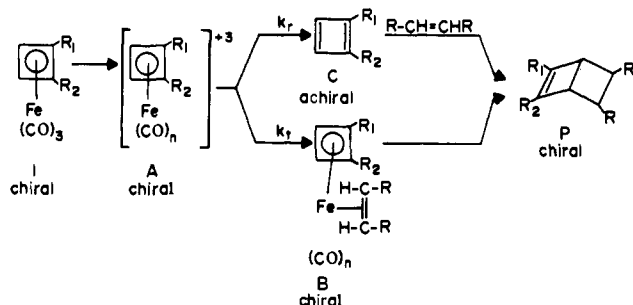
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The Mechanism of the Oxidative Decomposition of Cyclobutadienyliron Tricarbonyl Complexes: Intramolecular Trapping

Sir:

Cyclobutadienyliron tricarbonyl produces cyclobutadienoid intermediates on oxidative decomposition. Pettit and his co-workers¹ have demonstrated that these intermediates can be trapped to yield a large number of interesting products. Although cyclobutadiene has been generated photochemically² and observed at low temperatures, these complexes remain the best synthetic source of cyclobutadiene. Earlier studies suggested that "free" cyclobutadiene is produced on oxidation of cyclobutadienyliron complexes.^{3,4}

The possible schemes that were considered are:



It was shown that if an optically active cyclobutadiene complex (I) was decomposed in the presence of a symmetrical dienophile the products (P) were racemic. Since the cyclobutadiene (C) was the only reasonable achiral intermediate, these results suggested that the cyclobutadiene was released before reaction; i.e., $k_r \gg k_t$, in an intermolecular reaction.

Rebek⁵ applied the three phase test to this reaction. He demonstrated that cyclobutadiene was transferred through solution from a polymer containing the complex to another polymer containing a trapping agent. In this case k_t cannot be competitive with k_r .

We now have evidence that k_t is competitive with k_r under special conditions and that when the complexed intermediate is trapped, optically active products are produced. These results provide strong support for the results obtained earlier.^{3,4}

Cyclobutadienyliron tricarbonyl complexes containing dangling dienophiles have been observed to produce intramolecular trapping products in high yield.⁶

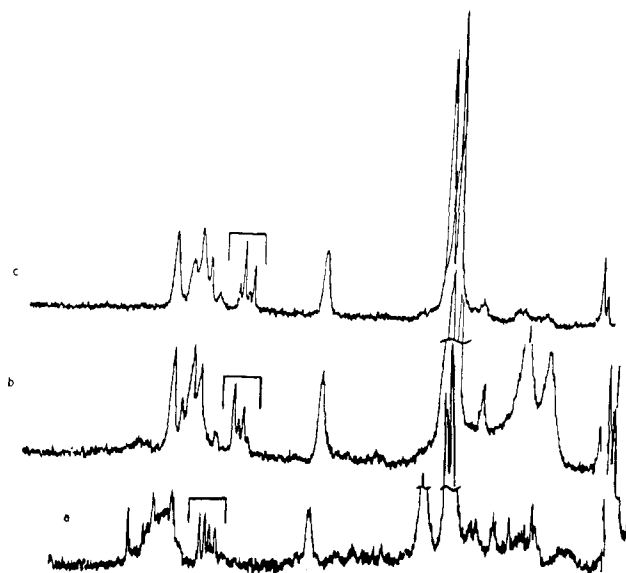
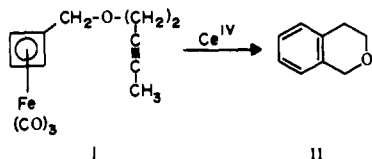
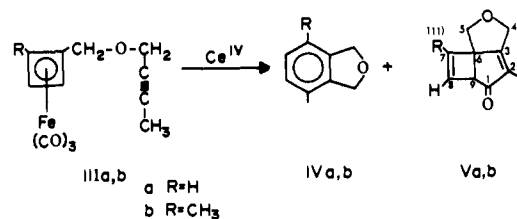
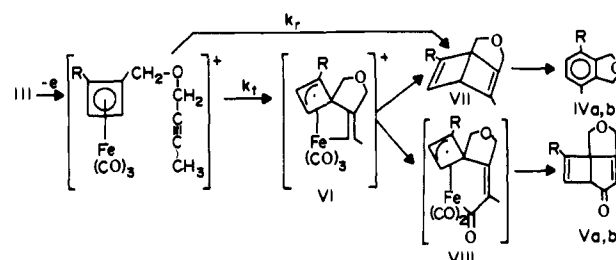


Figure 1. Optshifted spectra of Vb: (a) from racemic complex IIIb, (b) from (-) complex IIIb, (c) from (+) complex IIIb. The four peaks marked are produced from a doublet in the nonshifted spectra of IIIb.

When this reaction was carried out with the propargyl ether analogue (IIIa), two products were observed. The major product was the expected phthalan (80%) (IVa)⁷ and a minor product (Va) (15%)⁸ resulting from the insertion of carbon monoxide into the carbon framework of the ligand.



Past experience has shown that CO insertions only occur when a metal carbonyl is σ bound to a carbon. This suggested that in this case, k_t was competitive with k_r and the cyclobutadienoid was reacting while complexed to the metal. The products are best rationalized by the following scheme.



The intermediate VI is similar in structure to a series of neutral complexes prepared by Green and co-workers.⁹ Since the chain linking the diene and dienophile was short, the intramolecular trapping was competitive with the release of the ligand. However, once the intermediate (VI) was formed, reductive elimination to the Dewar benzene (VII) was inhibited due to the ring strain of the resulting system. Insertion of a carbon monoxide produced VIII and relieved sufficient strain for reductive elimination to occur to produce V.

To support this mechanism as well as to demonstrate that trapped cyclobutadienoid intermediates maintained chirality, IIIb was prepared and resolved. Oxidative decomposition (Ce^{IV}) of IIIb¹⁰ produced the methylated analogues IVb (75%) and Vb (20%).^{13,14} The experiment was repeated with optically active IIIb ($32 \pm 2\%$ optically pure). The resulting Vb, isolated