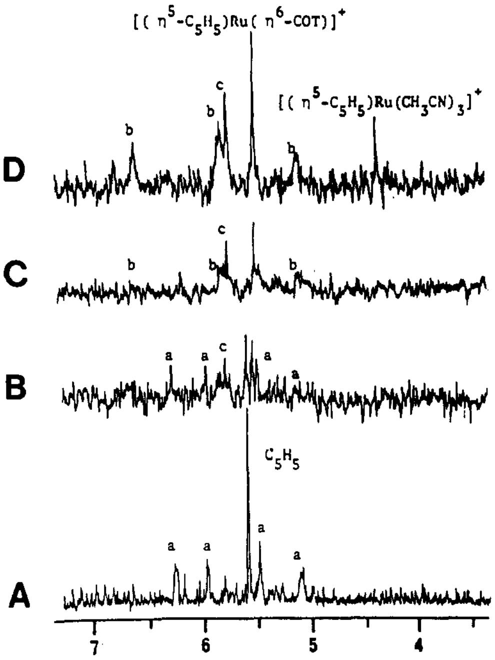

Figure 2. 79.5-MHz ^1H NMR spectra obtained during the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(CO)]PF_6$ in CD_3CN: A, before photolysis; B, after 1 min of photolysis; C, after 6 min of photolysis; D, after 16 min of photolysis. Peaks labeled a are due to the η^4-COT moiety in the starting complex. Peaks labeled b are peaks due to η^6-COT in one of the products, $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$. The peak labeled c is due to free COT.

from $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$ occurs too slowly (ie. 5% in 90 min) to be the source of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ in the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(CO)]^+$. Disappearance of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(CO)]^+$ is complete within 16 min of photolysis. Primary photochemical loss of η^4-COT is ruled out because no ^1H NMR peak is observed for the stable $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(CO)]PF_6$ complex.

To insure that the $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)^+$ formed in the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(CO)]^+$ was not formed via the synthetic reaction

$$[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+ + COT \rightarrow [(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+ + 3CH_3CN$$

the rate of this thermal reaction was studied. A 0.002 M solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$ was photolyzed with unfiltered light for 4 h and monitored by UV-vis spectroscopy for the appearance of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ (λ_{max} = 365 nm).[5] An absorbance change at 365 nm of 0.21 was observed after 4 h. The cell was then stored in the dark and monitored periodically for the loss of absorbance due to $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$. After 4 h, a change in absorption at 365 nm of 0.006 was observed, corresponding to less than 5% re-formation of the tris(acetonitrile) complex to form $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$. Data collected for the first 119 h of the recombination reaction exhibited (Figure 3) a linear dependence between $1/[[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+]$ and t (second order, equal concentration kinetics). From the slope, a second-order rate constant of 8.9 (0.4) $\times 10^{-3}$ M^{-1} s^{-1} was obtained. The small value for this rate constant indicates that the slow rate for photochemical release of COT from $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$ is not due to the competitive back reaction of COT with the tris(acetonitrile) complex.

Conclusions

In an attempt to observe the transformation from an η^6-COT to an η^4-COT configuration, solutions of $[(\eta^5\text{-}C_5R_5)M(\eta^6\text{-}COT)]^+$ were photolyzed under a variety of conditions. No evidence for stable η^4 intermediates was obtained in any of these experiments. $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(L)]^+$ (L = CO, $P(OCH_3)_3$) were photolyzed to observe the reverse $\eta^4 \rightarrow \eta^6$ transformation. When L = $P(OCH_3)_3$, η^4-COT is lost in the primary photochemical step to give $[(\eta^5\text{-}C_5H_5)Ru(P(OCH_3)_3)(CH_3CN)_2]^+$. In contrast, when L = CO, CO is lost in the primary step to give ultimately $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$ and $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$. The loss of η^4 COT from the putative intermediate $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)]^+$ is competitive with the $\eta^4 \rightarrow \eta^6$ collapse to form $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$. The slow back-reaction of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ and COT precludes the formation of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$ on the time scale of these experiments. Consequently the formation of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ in the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(CO)]^+$ does not occur via secondary photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$.

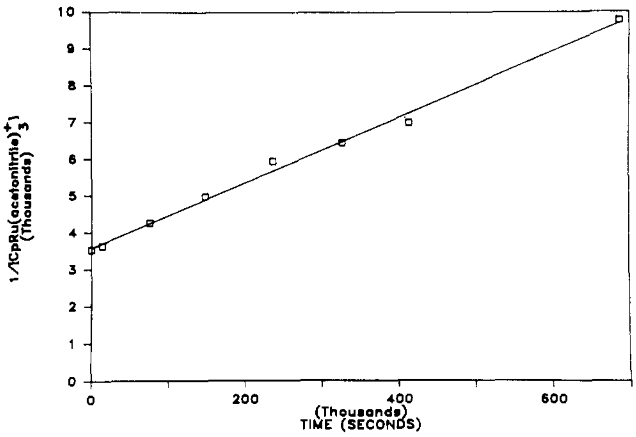

Figure 3. Plot of the reciprocal of $[[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+]$ vs. time for the 25 °C reaction of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ with COT. Squares represent experimental data; the least-squares line has intercept = 3580 M^{-1}, slope = 8.9 $\times 10^{-3}$ M^{-1} s^{-1}, and correlation coefficient = 0.9974.

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Registry No. $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}COT)]PF_6$, 79122-13-7; $[(\eta^5\text{-}C_5(CH_3)_5)Fe(\eta^6\text{-}COT)]PF_6$, 86991-94-8; $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]PF_6$, 80049-73-6; $[(\eta^5\text{-}C_5H_5)Fe(CH_3C(O)CH_3)_3]PF_6$, 101858-50-8; $[(\eta^5\text{-}C_5H_5)Fe(CH_3CN)_3]PF_6$, 99594-91-9; $[(\eta^5\text{-}C_5(CH_3)_5)Fe(CH_3CN)_3]PF_6$, 86991-88-0; $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$, 80049-61-2; $[(\eta^5\text{-}C_5H_5)Ru(P(OCH_3)_3)_3]PF_6$, 71397-30-3; $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)CO]PF_6$, 80049-75-8; $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(P(OCH_3)_3)]PF_6$, 101834-68-8; $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(P(OCH_3)_3)]PF_6$, 80049-65-6; $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$, 80049-60-1; $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$, 80049-72-5.

Contribution from the Department of Chemistry,
New Mexico State University, Las Cruces, New Mexico 88003

Rapid Pulse-Radiolytic Reduction of Iron(III) Complexes of Tetrakis(4-sulfonatophenyl)porphine Anion and Tetrakis(*N*-methylpyrid-4-yl)porphine Cation

P. C. Wilkins and R. G. Wilkins*

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Pulse radiolysis of water generates the primary radicals e_{aq}^-, H, and OH. With appropriate conditions each can be examined separately or used to produce other reducing or oxidizing radicals.[1] The distinct advantage of the technique is in the very rapid production of the radicals and, because of this, in the observation of very labile intermediates that may be produced in the interaction of the radicals with substrates.[1] The porphyrins and their metal complexes have been popular targets for this approach (For recent literature, see ref 2–12). Complexes of both naturally occurring

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Table I. Rate Constants for Reaction of Iron(III) Synthetic Porphyrins with Radicals

iron porphyrin	$10^{-10}k$, $M^{-1}\ s^{-1}$ e_{aq}^-	$10^{-10}k$, $M^{-1}\ s^{-1}$ CO_2^-
$Fe(TPPS)(H_2O)^{3-}$	3.8	0.18
$(Fe(TPPS))_2O^{8-}$	2.3	~0.2
$Fe(TMPyP)(OH)^{4+}$	6.9 (2.0)[a]	1.3 (0.75)[a]

[a] With 200 μM total iron, this is a mixture of dimer and monomer in 2 mM phosphate buffer.[6]

porphyrins (as model systems for heme proteins) as well as synthetic porphyrins have been studied. Reactivity toward reducing and oxidizing radicals has been examined, and both the metal center and the porphyrin ring have been the focus of attention.

We have recently examined the monomer–dimer equilibrium involving the iron(III) complexes of the water soluble tetrakis(4-sulfonatophenyl)porphine anion (H_2TPPS^{4-}) and tetrakis(*N*-methylpyrid-4-yl)porphine cation (H_2TMPyP^{4+}) and have characterized spectrally the various species present and their interconversion rates.[13,14] The reactions of these iron complexes with pulse radiolytically produced radicals have been little examined, with focus mainly on reactivity towards O_2^- and superoxide dismutase activity.[4,6] We describe here the reactions of e_{aq}^- and CO_2^- with the monomers $Fe(TPPS)(H_2O)^{3-}$ and $Fe(TMPyP)(OH)^{4+}$ and with the dimer $(TPPS)Fe–O–Fe(TPPS)^{8-}$, examining, in particular, the nature of the products.

Experimental Section

Tetrasodium *meso*-tetrakis(4-sulfonatophenyl)porphine dodecahydrate and *meso*-tetrakis(*N*-methylpyrid-4-yl)porphine tetraiodide were purchased from Strem Chemicals. The iron complexes were prepared as described in the literature.[13-16] A CN Van de Graaff electron accelerator at the Center for Fast Kinetics Research was used as an electron source. Pulses of 100-ns duration were delivered to samples in a quartz cell (1-cm optical path length), and absorptions of species produced were monitored by using a conventional xenon lamp, monochromator, and photomultiplier. The signals were digitized by a Biomation 8100 transient recorder and analyzed by using an on-line PDP 11/70 minicomputer. The reactions of the electron were studied by inclusion of 1% *tert*-butyl alcohol, which removes H and OH radicals by converting them to the relatively unreactive radical $\cdot CH_2(CH_3)_2OH$.[1] If 50 mM formate and saturated N_2O were used in place of 1% *tert*-butyl alcohol, then all primary radicals were converted into CO_2^- radicals by (1) and (2). The concentrations

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH + OH^- \qquad (1)$$

$$OH/H + HCO_2^- \rightarrow H_2O/H_2 + CO_2^- \qquad (2)$$

of radicals were 3–6 μM, and the iron complexes varied from 10 to 50 μM (in terms of iron(III) concentration). Reactions were carried out at pH 5–9 by using phosphate buffers. The concentration of e_{aq}^- was estimated from the absorbance change at 650 nm ($\epsilon(e_{aq}^-) = 1.6 \times 10^4\ M^{-1}\ cm^{-1}$). The concentration of CO_2^- generated was approximately twice that of the e_{aq}^- produced with the same conditions. The accurate value was assessed from the known overall spectral change for Fe(III) to Fe(II) porphyrin conversion. All experiments were carried out with the rigorous exclusion of oxygen by using a N_2 or N_2O atmosphere.

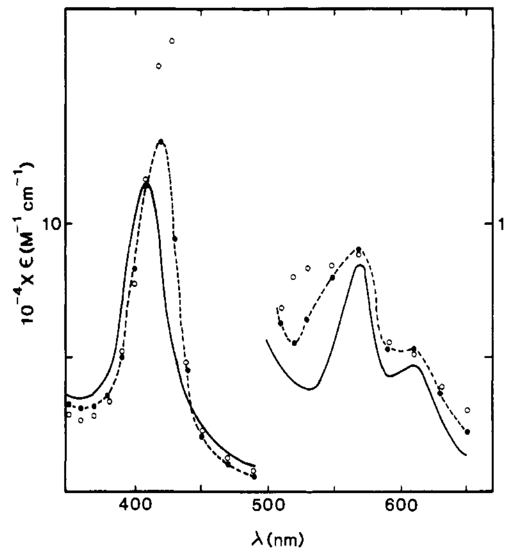

Figure 1. Spectra of $(Fe(TPPS))_2O^{8-}$ (—) and e_{aq}^--reduced product (solid circles and ---) at 8.5 μs after pulse initiation. The latter was obtained from the difference spectrum at 8.5 μs after 10 μM dimer was reacted with 3.2 μM e_{aq}^- at pH 9. The open circles represent $^1/_2(\epsilon_{Fe(III)} + \epsilon_{Fe(II)})$, where the absorbance coefficients are for $Fe(TPPS)(OH)^{4-}$ and $Fe(TPPS)(OH)^{5-}$, respectively, at pH 9. The absorbance coefficients for the dimer are in terms of the *total* iron concentration.

The iron(II)–TPPS species was prepared by adding a slight excess of dithionite to the iron(III) complex and permitting the mixture to stand for 15 min to allow complete reduction. A stock solution of the iron(II)–TPPS complex (5–10 mM) was added to buffer at various pH (4.5–9.0) or to different volumes of buffer at pH 8.0, and the spectra were determined. A small amount of dithionite was added to the buffer to maintain the iron(II) forms.

Results and Discussion

If the iron(III) porphyrins are used in excess of the generated e_{aq}^- or CO_2^-, there is a first-order loss of iron(III) porphyrin. The observed rate constant k_{obsd} is independent of the wavelength of examination, which included 650 nm, where the loss of e_{aq}^- is specifically monitored. The slope $\Delta k_{obsd}/\Delta$ [iron(III)porphyrin] gave the second-order rate constants shown in Table I for the reaction of the two radicals. There is a small effect of the charge of the iron complex on the rate constant for its reaction with e_{aq}^- although the value for $Fe(TMPyP)(OH)^{4+}$ is higher than that found for most iron(III) porphyrins[1] and myoglobins[7] ($\sim 2 \times 10^{10}\ M^{-1}\ s^{-1}$). There is a much larger effect of the charge on the reaction with the less powerful CO_2^-, the rate constant for the positively charged iron–TMPyP complex being almost 10 times that for the negatively charged species in Table I. A similar accelerated rate toward $(CH_3)_2\dot{C}O^-$ has been observed for TMPyP complexes of Co(III)[3] and Zn(II),[3] but not Mn(III),[10] compared with those of TPPS.

Difference spectra (product − reactant) were obtained for the immediate product of the reduction, as well as for any subsequent changes. The wavelength range examined was dictated by suitably low background absorbances and a relatively high [iron]/[radical] ratio to maintain one-electron reduction.

$Fe(TPPS)(OH_2)^{3-}$ and $(TPPS)Fe–O–Fe(TPPS)^{8-}$. It is established that these are the predominant species at pH 5 and 9, respectively.[14,15] Reaction at pH 5 of 50 μM $Fe(TPPS)(OH_2)^{3-}$ with 3 μM e_{aq}^- or ~6 μM CO_2^- gave a difference spectrum between the product and the reactant at 5 or 65 μs (when reduction by e_{aq}^- or CO_2^-, respectively, was complete), which corresponded very well to that expected from the known spectra of $Fe(TPPS)(OH_2)^{3-}$ and the dithionite-produced iron(II) product at pH 5.[17] There was a subsequent slower change after the e_{aq}^- had

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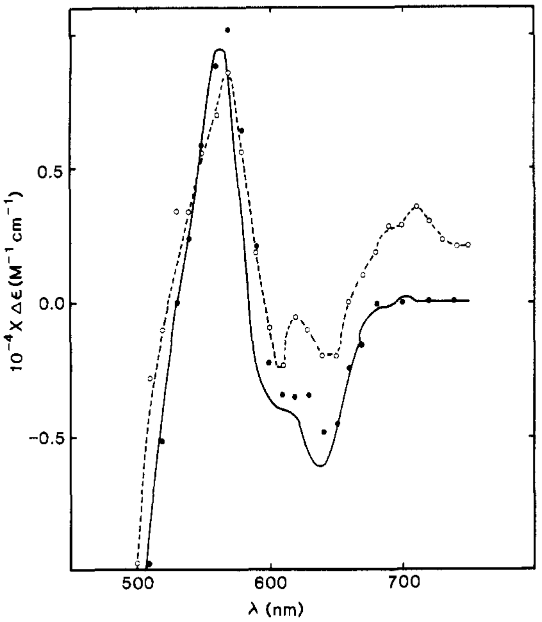

Figure 2. Plots of the molar absorbance coefficients differences for product minus reactant from reduction of 20 μM $Fe(TMPyP)(OH)^{4+}$ by 6.0 μM CO_2^- in 50 mM formate at pH 8.0. Open and solid circles represent completion of CO_2^- loss (20 μs) and completion of the slow reaction (1500 μs), respectively. The full line represents the calculated difference spectrum, from the known spectra for $Fe(TMPyP)(OH)^{4+}$ and the (chemically reduced) iron(II) product.

disappeared ($k \sim 5 \times 10^3$ s^{-1}). The absorbance changes were very small and continued in the same direction (loss or gain at various wavelengths) as was produced initially by e_{aq}^-. The absorbance changes were ascribed to further slower reduction of $Fe(TPPS)(OH_2)^{3-}$, perhaps by $\cdot CH_2C(CH_3)_2OH$, a complication previously considered with e_{aq}^- reduction of the Co(III)–TMPyP complex.[3] This slow reaction was not observed when CO_2^- was used, lending support to this explanation.

The spectra of the dimer $(TPPS)Fe–O–Fe(TPPS)^{8-}$ and of the product of the e_{aq}^- reduction (obtained from difference spectra at 8 μs after pulse) are shown in Figure 1. We have calculated the absorbance of a mixture of iron(III) and iron(II) species that would result from reactions 3 and 4. The iron(III) species present

$$(TPPS)Fe^{III}–O–Fe^{III}(TPPS)^{8-} \xrightarrow{e_{aq}^-} (TPPS)Fe^{III}–O–Fe^{II}(TPPS)^{9-} \quad (3)$$

$$(TPPS)Fe^{III}–O–Fe^{II}(TPPS)^{9-} \rightarrow (TPPS)Fe^{III}(OH)^{4-} + (TPPS)Fe^{II}(OH)^{5-} \quad (4)$$

at pH 9 is the monohydroxy species, the spectrum of which has been obtained by rapid-scan stopped-flow spectrophotometry.[13] The monohydroxy species only transforms to the dimer slowly (in seconds at pH 9). We consider that the iron(II) species is also a monohydroxy monomer at pH 9, as the result of some spectral work. The spectra (500–700 nm) of the iron(II) species are identical at pH 9, with concentrations ranging from 8.9 to 147 μM, almost certainly precluding any dimer formation. Further, a series of Soret spectra at pH 4.5–9.0 show an isosbestic point at 415 nm and $pK_a \sim 5.2$. The calculated absorbances are in reasonable agreement with those determined experimentally (Figure 1). Some differences arise, undoubtedly from the error in measuring small absorbance changes in the visible region and partly from the large absorbance background in the Soret region. In addition, with the relatively low concentrations of dimer that had to be used (~10–25 μM), there will be 15–30% hydroxy monomer present,[13] some of which will react with e_{aq}^- to give solely iron(II). A similar difference spectrum was obtained when CO_2^- was used, but the reduced reactivity did not allow for as early an examination of the primary product, and slower first-order changes ($k = 8 \times 10^3$ s^{-1} independent of wavelength and 10–25 μM dimer) interfered with its collection. The slower changes probably involved reactions of the fragments and were not further examined.

Unless it is assumed that the spectrum of the mixed iron(II)–iron(III) species will be a composite of the iron(II) and iron(III) monomers, which is highly unlikely, it is clear that the iron(II)–iron(III) dimer first formed in (3) dissociates to fragments within 6 μs (4), setting the first-order rate constant for dissociation at $>10^6$ s^{-1}. The contrast with the dissociation of the iron(III)–iron(III) dimer ($k \sim 10^{-2}$ s^{-1} at pH = 9)[13] is striking. There appears to be little information on the stability in water of porphyrin dimers containing either one or two iron(II) atoms. Evidence for semireduced and fully reduced $[(TPP)Fe]_2O$ and $[(CN)_4TPPFe]_2O$ in DMF, without destruction of the dimer, has been obtained by Kadish et al.[18,19] from electrochemical and spectral observations.

$Fe(TMPyP)(OH)^{4+}$. The behavior with this species present at pH 8[14] differs from that with $Fe(TPPS)(OH_2)^{3-}$, in that an intermediate is produced at the end of the CO_2^- reaction (20 μs) with marked absorbance at ~700 nm (Figure 2). Such a transient was not reported previously.[6] The transient disappears in a first-order fashion ($k = 2.3 \times 10^3$ s^{-1}) to a final spectrum which is quite close[14] to that of $Fe(TMPyP)^{4+}$ (Figure 2). A similar rate constant was obtained with different iron(III) concentrations (6.7–20 μM) and observation wavelengths. The slow change is different in character from that observed with $Fe(TPPS)(OH_2)^{3-}$, and we ascribe it to the transfer of an electron from a porphyrin radical (produced by some of the CO_2^-) to iron(III). The reactions of metal-free H_2TMPyP[5] and deuteroporphyrin[9] with $(CH_3)_2\dot{C}O^-$ are reported to give transients with absorbance peaks at ~730 and ~630 nm ($\epsilon \sim 10^4$ M^{-1} cm^{-1}), and these are considered to be porphyrin radicals. Transients with similar absorbance characteristics in the 700–750-nm region are also observed in some (but not all[2,12]) radical reductions of porphyrin complexes of metals in non easily reduced oxidation states such as Sn(IV),[11] Al(III),[8,11] Mn(II),[10] Zn(II),[3] and Fe(II) (in myoglobin and derivatives[7]). The reduction of $Co^{III}(TMPyP)^{5+}$ by $(CH_3)_2\dot{C}O^-$ at pH 13 gave transients with excess absorbance at 700–750 nm ($\epsilon \sim 2 \times 10^3$ M^{-1} cm^{-1}), suggesting production of some Co^{III} $(TMPyP^-)^{5+}$, which disappeared over ~1 s.[3] This direct attack on the porphyrin was not observed with $Co^{III}(TPPS)^{3-}$, perhaps becase of the absence of positive charge. A similar difference was shown here by the iron(III) complexes of H_2TMPyP^{4+} and H_2TPPS^{4-}. The nature of the spectral changes and the value of Δε's at ~700 nm suggest that *most* of the CO_2^- radicals react directly with the iron(III). The rapid transfer of electrons from Fe(III)-coordinated $TMPyP^-$ to Fe(III) is understandable. It was not possible to examine $(TMPyP)Fe–O–Fe(TMPyP)^{8+}$ since the dimerization constant is small (2.6×10^3 M^{-1} at pH 8.0) and even 100 μM (iron concentration) contains substantial amounts of monomeric $Fe(TMPyP)(OH)^{4+}$ (~70%). This would interfere markedly with the analysis of the results.

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Registry No. $Fe(TPPS)(H_2O)^{3-}$, 53194-20-0; $(Fe(TPPS))_2O^{8-}$, 64365-01-1; $Fe(TMPyP)(OH)^{4+}$, 97889-58-2; CO^{2-}, 14485-07-5; H_2O, 7732-18-5.

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