Table I

I_0, einstein cm^{-2} s^{-1} × 10^9	conversion	ϕ_{cor}	
		eq 1	eq 2
3.5	high	0.50	0.65
3.5	high	0.41	0.56
1.43	high	0.29	0.45
3.5	low	0.38	0.45
3.5	low	0.38	0.44

of two of the plots is to be seen also in Simmons's published data.[10]

Equation 1 should have about $^2/_3$ the slope of eq 2, and for the higher conversions this prediction is obeyed well. For the lower conversions the factor is closer to 0.5. Equation 3 would be expected to yield values similar to those of 1 for low conversions, but instead it yields values closer to those of 2. In addition it shows a time dependence quite different from the other expressions. Since eq 1 and 2 seem to be in quite good agreement, we have based our quantum yield determinations on them. Table I shows quantum yields obtained by fitting the results to the best straight line for both low and high conversions at two monochromatic light intensities. The quantum yields have been corrected to take account of the fact that irradiation was at 436 nm where the sample has a constant, smaller reflectance than at 520 nm where the reflectance changes were analyzed. Since the light flux at the sample surface is proportional to $1 + R^2$, a correction factor $(1 + R_{436}^2)/(1 + R_{520}^2)$ was applied to the absorbed light intensity. This had the effect of reducing the quantum yields by 30%.

The quantum yields of Table I range from 0.29 to 0.65. The lowest value found, but not shown in the table, 0.26, is obtained from the zero time tangent to the plot of eq 1. Although there is a fairly large, and difficult to assess, uncertainty in these values, they confirm the qualitative observation that this is a rather efficient solid-state photoaquation. It is particularly interesting that the value is of the same order as the solution photoaquation yield[12] of 0.27, an observation reminiscent of the situation reported for photoredox reactions in some oxalate complexes.[13]

It is unfortunate that the single-crystal X-ray structure of this monohydrate salt has not been reported. It might have proved interesting to see whether the water of crystallization is particularly favorably disposed toward entry into the coordination sphere. It is, to us, a particularly interesting observation that the photoaquation apparently obeys the same photostereochemical selection rules that apply in solution. Clearly in the solid there is ample room for rearrangement throughout the course of substitution of the excited state.

We found that the photoaquation yield dropped by a factor of 10 on cooling to liquid-nitrogen temperature but photolysis still occurred. In this respect, the behavior is similar to recent observations for frozen solutions,[7] where it was found that some glassy solution environments remain photochemically active down to low temperature. It may be that in a crystal the low-temperature process involves defects and dislocation sites.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC), the University of Victoria, and the Government of British Columbia for financial support for this work.

Registry No. *trans*-$[Cr(en)_2Br_2]Br{\cdot}H_2O$, 30852-95-0; *trans*-$[Cr(en)_2Br_2]NCS$, 94499-31-7; *trans*-$[Cr(en)_2Br_2]ClO_4$, 28074-55-7; *trans*-$[Cr(en)_2Br_2]NO_3$, 94499-32-8; *trans*-$[Cr(en)_2Br_2]Br$, 14240-27-8; *trans*-$[Cr(en)_2Br_2]I$, 94499-33-9; *trans*-$[Cr(en)_2Br_2]NCO$, 94499-34-0; *trans*-$[Cr(en)_2Br_2]Ag(CN)_2$, 94499-36-2; *trans*-$[Cr(en)_2Cl_2]Cl$, 14301-97-4; *trans*-$[Cr(en)_2Cl_2]Cl{\cdot}H_2O$, 94499-37-3; *trans*-$[Cr(en)_2F_2]Cl$, 19581-00-1; *trans*-$[Cr(en)_2(NCS)_2]ClO_4$, 43176-07-4; *cis*-$[Cr(en)_2BrH_2O]^{2+}$, 60429-48-3; *cis*-$[Cr(en)_2NCSH_2O]^{2+}$, 25078-44-8; *trans*-$[Cr(en)_2BrH_2O]^{2+}$, 17979-12-3; *trans*-$[Cr(en)_2NCSH_2O]^{2+}$, 25125-60-4.

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Contribution from the Department of Chemistry,
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Photodisproportionation of (μ-Oxo)bis((tetrakis(4-carboxyphenyl)porphinato)iron(III))

MARK W. PETERSON and ROBERT M. RICHMAN*

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The water-soluble complex (μ-oxo)bis((tetrakis(4-carboxyphenyl)porphinato)iron(III)) has been synthesized and characterized. Its photochemistry has been studied in the presence of reductive amines. Continuous photolysis in the presence of either EDTA or TEOA results in the two-electron oxidation of the amine with a strongly wavelength-dependent quantum yield. The observed quantum yield at 409 nm is 5.2×10^{-5}, about half the 1.0×10^{-4} value measured for the aprotic-soluble analogue $(FeTPP)_2O$. Flash photolysis confirms that the primary photoprocess is disproportionation and that the oxidation of amines by the ferryl complex is complete within 100 ns.

Introduction

Recently we reported that (μ-oxo)bis((tetraphenylporphinato)iron(III)) ($(FeTPP)_2O$) will photochemically disproportionate to yield the ferrous and ferryl complexes. The ferryl complex represents a strong one-electron oxidant that may be trapped by triphenylphosphine.[1]

$$(FeTPP)_2O \xrightarrow{h\nu} FeO(TPP) + FeTPP$$

$$FeO(TPP) + PPh_3 \rightarrow FeTPP + OPPh_3$$

This photoreaction represents an alternative approach to the conventional use of long-lived excited states to generate strong oxidants.[2-4] Perhaps the most discouraging aspect of that work was the small quantum yield obtained ($\phi_0 = 1.0 \times 10^{-4}$). This quantum yield no doubt reflects the effects of primary (cage) and secondary recombination, and hence the absolute quantum yield may well be substantially higher. The nature of the excited state responsible for this photoreaction also remains in question.

There has been much interest in the photochemical conversion of sunlight to useful energy, with much attention being paid to the splitting of water. We have begun the study of a water-soluble μ-oxo-bridged complex, (μ-oxo)bis((tetrakis(4-carboxyphenyl)porphinato)iron(III)) ($(FeTPPC)_2O$). It was anticipated that the quantum yield should increase since the products would be

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0020-1669/85/1324-0722$01.50/0

charged, and hence Coulombic repulsion should inhibit cage recombination. Here we report the synthesis, characterization, and photochemistry of $(FeTPPC)_2O$ in the presence of amines. The photochemistry is characterized by photodisproportionation with a strongly wavelength-dependent quantum yield that is actually lower than that of $(FeTPP)_2O$ at 409 nm and a two-electron transfer from the ferryl complex to amines within 100 ns.

Experimental Section

Compounds and Materials. $(FeTPPC)_2O$ was prepared in a manner analogous to the preparation of FeTPP with the exception of allowing O_2 into the reaction vessel after refluxing.[5] (FeTPPC)Cl was prepared by acidifying (HCl) a DMF solution of $(FeTPPC)_2O$. FeTPPC was prepared by dithionite reduction of (FeTPPC)Cl.

Disodium ethylenediaminetetraacetate (EDTA), α-4-pyridyl-*N-tert*-butylnitrone *N′*-oxide (POBN), NaOD (30% solution in D_2O), and D_2O were obtained from Aldrich Chemical Co. and used without further purification. Spectral grade pyridine obtained from Aldrich was periodically distilled. Triethanolamine (TEOA, 97%) obtained from Aldrich was vacuum distilled prior to use.

Quantum Yield Determination. All quantum yields were determined in buffered water. The pH was maintained between 9 and 10. Since FeTPPC represents the ultimate photoproduct and is extremely O_2 sensitive, all samples were freeze–pump–thaw degassed through a minimum of three cycles. All quantum yields reported have been corrected for internal filtering and low absorption of the photoactive complex.[1]

Instrumentation. Irradiations were performed with a Hanovia 1000-W mercury–xenon lamp using a Bausch and Lomb high-intensity monochromator. Spectral changes were monitored on a Perkin-Elmer Model 330 UV–visible spectrophotometer that is interfaced to a Perkin-Elmer CDS-2 data station. IR spectra were recorded on a Perkin-Elmer Model 580 spectrophotometer. NMR spectra were recorded on a Bruker WM-300 300-MHz NMR spectrometer.

Flash Photolysis. Transient spectra were obtained at the Regional Laser Laboratories at the University of Pennsylvania. The spectra were recorded between 550 and 350 nm by using the third harmonic (355 nm) of a Quanta-Ray DCR Nd:YAG pulsed laser for excitation of an EG&G Xe flash lamp as a probe. Spectra were recorded from 58 ns to 50 μs by using a PAR 1211 instrument to trigger a Silicon Intensified Vidicon that recorded the light transmitted onto an American ISA spectrograph. The resultant spectra were digitized (PAR Model 1216) and manipulated on a Digital Equipment Corp. MINC-11 computer to produce the ultimate difference spectra.

Samples were prepared in buffered water under argon and then placed in either a 0.1- or 0.2-cm quartz cell and purged with argon. All samples were mixed after excitation and replaced after about 10 runs to prevent any permanent products from building up in local areas.

Results and Discussion

The complex $(FeTPPC)_2O$ is readily soluble in water at pH ≥ 8. Its electronic absorption spectrum is similar to those of both $(FeTPP)_2O$ and the sulfonated $(FeTPPS)_2O$,[6] with λ_{max} ($\epsilon \times 10^{-4}$) = 318 (6.0), 409 (16.6), 567 (1.3), and 609 nm (0.81) in the pH range of 8–11. When this complex is dissolved in slightly acidic organic solvents, the spectrum resembles those of Fe^{III}TPPS and (FeTPP)Cl with λ_{max} ($\epsilon \times 10^{-4}$) = 376 (6.3), 418 (11.9), and 509 nm (1.5). Magnetic susceptibility measurements in pH 10 water give a moment of 2.84 μ_B, similar to that expected for a water-soluble μ-oxo-bridged dimer.[6] An infrared absorption (KBr) is found at 863 cm^{-1} compared to 878 cm^{-1} for $(FeTPP)_2O$ and 872 cm^{-1} for $(FeTPPS)_2O$. Its NMR spectrum consists of the pyrrole resonance at δ 13.7 (8 H), the ortho resonances at δ 8.25 and 8.2 (8 H), and the meta resonance at δ 7.6 (8 H). These results firmly establish that this complex is in the form of a μ-oxo-bridged dimer in aqueous base as opposed to a monomeric hydroxide.[7]

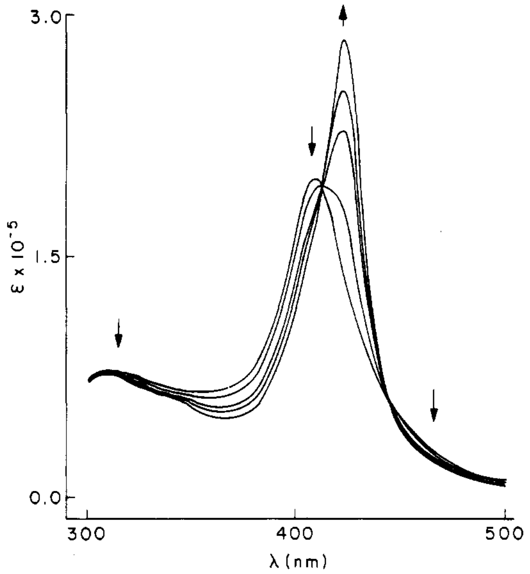

Figure 1. Spectra of the photolysis of $(FeTPPC)_2O$ in pH 10 buffer in the presence of 0.1 M TEOA; excitation at 365 nm; spectra taken at t = 0, 2, 4, 6 and 8 min of irradiation.

Photolysis of this complex in the pH range 9–11 in the presence or absence of phosphate or borate buffers leads to no spectral changes; however, if a commercial buffer is used, a clean photoreduction to Fe^{II}TPPC occurs. It was readily determined that the mold inhibitor in the commercial buffer, EDTA, was the active trap. Since amines are prone toward radical reactions, TEOA was chosen as the trapping agent for photostudy since its radical reaction products have been characterized at several pHs:[8-10]

$$R_2N(CH_2CH_2OH) \rightarrow R_2N(CH_2CH_2OH)^+ + e^-$$

at pH >9: $R_2N(CH_2CH_2OH)^+ \rightarrow R_2N{=}CHCH_2OH + H^+$

The deprotonated form is a strong reductant with two possible paths of decomposition:

path 1

$$R_2N{=}CHCH_2OH \rightarrow R_2N(CH_2CHO) + e^- + H^+$$

path 2

$$R_2N{=}CHCH_2OH \rightarrow R_2N{=}CHCH_2OH^+ + e^-$$

$$H_2O + R_2N{=}CHCH_2OH^+ \rightarrow R_2NH + CH_2OHCHO + H^+$$

The spectral changes accompanying photolysis of a 0.1 M TEOA solution of $(FeTPPC)_2O$ at 409 nm are shown in Figure 1. FeTPPC can be seen growing in at 427 nm ($\epsilon = 2.01 \times 10^5$ M^{-1} cm^{-1}) while the peaks due to $(FeTPPC)_2O$ diminish. Isosbestic points are maintained at 442 and 412 nm. This reaction was scaled up to 2.0×10^{-3} M $(FeTPPC)_2O$ and photolyzed for about 10 h with a 450-W medium-pressure mercury lamp. The resulting solution tests positive for glycolaldehyde.[9,11] The NMR spectrum of this sample shows the presence of $HN(CH_2CH_2OH)_2$. Comparison of the integrated pyrrole peak due to $(FeTPPC)_2O$ (δ 13.7) and the OH peak of $HN(CH_2CH_2OH)_2$ (δ 3.87) implies quantitative conversion within experimental error (i.e., the ratio of the loss of $(FeTPPC)_2O$ to the gain of $HN(CH_2CH_2OH)_2$ is 0.95 ± 0.05). No evidence is found for formation of ONR_3.

The potential mechanisms are the same as those discussed for $(FeTPP)_2O$.[1] Electron-transfer quenching is eliminated on the basis of the lack of emission of $(FeTPPC)_2O$ below 800 nm at room temperature. Furthermore, the quantum yield varies neither with the concentration of trap nor with the nature of the trap (ϕ_o(EDTA) = ϕ_o(TEOA) at 409 nm).

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Formation of a precursor complex is eliminated on the basis of the lack of UV–visible spectral changes upon addition of TEOA or EDTA and the lack of any changes in the NMR spectrum of either TEOA or $(\text{FeTPPC})_2\text{O}$ upon mixing of equimolar solutions.

Dissociation to FeTPPC^+ and FeO(TPPC)^- can be eliminated since monomeric $\text{Fe}^{\text{III}}\text{TPPC}$ shows no reaction with TEOA at low pH.

The conclusion may be drawn that this complex is, as with $(\text{FeTPP})_2\text{O}$, photodisproportionating. The exact route by which FeTPPC is being produced could be quite complex owing to the radical nature of the decomposition of TEOA. The potential reactions are

$$\text{FeO(TPPC)} + \text{TEOA} \rightarrow \text{FeO(TPPC)}^- + \text{TEOA}^+ \quad (1)$$

$$\text{FeO(TPPC)}^- + \text{TEOA}^+ \rightarrow \text{FeO(TPPC)} + \text{TEOA} \quad (2)$$

$$\text{TEOA}^+ \rightarrow \text{TEOA}' + \text{H}^+ \quad (3)$$

$$\text{FeO(TPPC)}^- + \text{TEOA}' \rightarrow \text{FeTPPC} + \text{H}_2\text{O} + \text{products} \quad (4)$$

$$(\text{FeTPPC})_2\text{O} + \text{TEOA}' \rightarrow \text{Fe}^{\text{II}}(\text{TPPC})\text{OFe}^{\text{III}}\text{TPPC} + \text{products} \quad (5)$$

where TEOA′ is $\text{R}_2\text{N}{=}\text{CHCH}_2\text{OH}$.

Step 5 may be eliminated since there is no spectral evidence for formation of the mixed-valence $(\text{Fe}^{\text{II}}\text{TPPC})\text{–O–}(\text{Fe}^{\text{III}}\text{TPPC})$[12] on either a continuous- or flash-photolysis time scale. In fact from path 1 a mechanism for the two-electron reduction of FeO(TPPC) can be derived that is independent of pH:

Mechanism I

$$\text{FeO(TPPC)} + \text{TEOA} \rightarrow \text{FeO(TPPC)}^- + \text{TEOA}^+ \quad (6)$$

$$\text{FeO(TPPC)}^- + \text{TEOA}^+ \rightarrow \text{FeO(HTPPC)} + \text{R}_2\text{N}{=}\text{CHCH}_2\text{OH} \quad (7)$$

$$\text{FeO(HTPPC)} + \text{R}_2\text{N}{=}\text{CHCH}_2\text{OH} \rightarrow \text{FeTPPC} + \text{R}_2\text{NH} + \text{CHOCH}_2\text{OH} \quad (8)$$

$$\text{net:}\quad \text{FeO(TPPC)} + \text{TEOA} \rightarrow \text{FeTPPC} + \text{R}_2\text{NH} + \text{CHOCH}_2\text{OH} \quad (9)$$

Alternatively, the same products may be produced by an oxo atom transfer reaction followed by either photochemical or thermal decomposition of the resulting amine oxide:

Mechanism II

$$\text{FeO(TPPC)} + \text{TEOA} \rightarrow \text{FeTPPC} + \text{R}_3\text{N–O} \quad (10)$$

$$\text{R}_3\text{N–O} \rightarrow \text{R}_2\text{NH} + \text{CHOCH}_2\text{OH} \quad (11)$$

The result would be the same as step 9. A photochemical step (eq 11) may be eliminated since there is no observable absorption by the organic products at the excitation wavelength and no transient evidence for formation of R_3NO. Thermal decomposition also seems unlikely since most known amine oxides are thermally stable at ambient temperatures.

Mechanism I for the two-electron transfer to FeO(TPPC) from TEOA seems reasonable despite the fact that prolonged photolysis of a solution of $(\text{FeTPPC})_2\text{O}$ and TEOA or EDTA in the presence of the ESR spin trap POBN leads to no detectable ESR signals, because any radicals being produced could be very short-lived. This then leads to a mechanism comparable to the PPh_3 reaction with $(\text{FeTPP})_2\text{O}$.[1]

$$(\text{FeTPPC})_2\text{O} \xrightarrow{h\nu} (\text{FeTPPC})_2\text{O}^* \quad (12)$$

$$(\text{FeTPPC})_2\text{O}^* \rightarrow \text{FeTPPC} + \text{FeO(TPPC)} \quad (13)$$

$$\text{FeTPPC} + \text{FeO(TPPC)} \rightarrow (\text{FeTPPC})_2\text{O} \quad (14)$$

$$\text{FeO(TPPC)} + \text{TEOA} \rightarrow \text{FeTPPC} + \text{R}_2\text{NH} + \text{CHOCH}_2\text{OH} \quad (15)$$

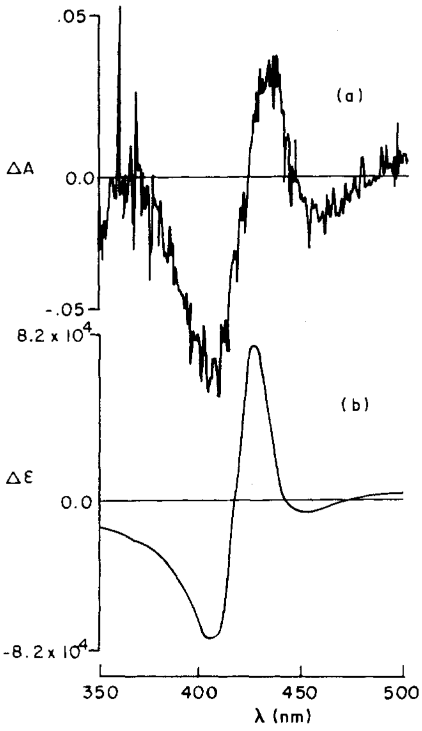

Figure 2. (a) Transient absorption spectrum of $(\text{FeTPPC})_2\text{O}$ in pH 10 buffer; spectrum recorded 100 ns after excitation at 355 nm. (b) Difference spectrum of $(\text{FeTPPC})_2\text{O}$ – FeTPPC.

where eq 9 has been assumed to be correct. Hence the quantum yield should follow the relationship

$$1/\phi_{\text{obsd}} = 1/2\phi_0 + [\text{FeTPPC}]k_{14}/2\phi_0 k_{15}$$

Unfortunately this equation is of little value in this case. It is found that the quantum yield shows no variation with irradiation time (within experimental error) at high concentrations of trap ($[\text{TEOA}] > 0.005$ M) and no simple variations at low concentrations of trap ($[\text{TEOA}] < 0.0001$ M). This may be explained in two ways: (1) the back-reaction (k_{14}) is being inhibited by coordination of the amine or (2) the trapping rate (k_{15}) is sufficiently large so that $k_{14}/k_{15} \sim 0$. Coordination by TEOA seems unlikely since it has been observed that dicoordination of FeTPPC (either with pyridine or piperidine) hinders its reaction with O_2 while FeTPPC remains extremely O_2 sensitive in the presence of only TEOA.

It should be noted that short-wavelength photolysis of $(\text{FeTPPC})_2\text{O}$ in the presence of both a trap and pyridine leads to a higher quantum yield than in the absence of pyridine. This at first seems puzzling; however, Hoffman and co-workers demonstrated that paraquat and either EDTA or TEOA will form a complex that is photoactive in the short-wavelength region, leading to the formation of the appropriate radicals.[8] We therefore speculate that pyridine is acting in the same role as paraquat and the radicals so generated may then attack $(\text{FeTPPC})_2\text{O}$.[13]

Flash photolysis of $(\text{FeTPPC})_2\text{O}$ supports the photodisproportionation mechanism. Figure 2a shows the transient absorption spectrum obtained 100 ns after excitation of a pH 10 solution of $(\text{FeTPPC})_2\text{O}$. Figure 2b shows the difference spectrum obtained by subtracting equimolar concentrations of FeTPPC from $(\text{FeTPPC})_2\text{O}$. It is seen that these two difference spectra are identical in both the peak positions of bleaching and growth and the relative intensities. While the short-wavelength region is not resolved, it is possible that the ferryl complex absorbs in this region (it is noted

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(13) Addition of EDTA to a pH 10 solution of pyridine causes a slight enhancement of the pyridine spectrum at long wavelengths (280 nm < λ ≲ 400 nm). No consistent photochemical changes are observed in the UV–visible spectrum upon irradiation of such a solution; however, photolysis in the presence of the ESR spin trap POBN leads to the production of two highly convoluted signals typical of trapped radicals.

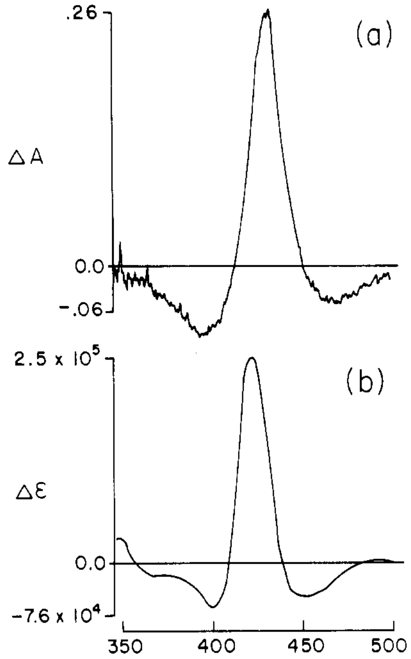

Figure 3. (a) Transient absorption spectrum of $(FeTPPC)_2O$ in pH 10 buffer in the presence of 0.1 M TEOA; spectrum recorded 100 ns after excitation at 355 nm. (b) Difference spectrum of $(FeTPPC)_2O$ − 2FeTPPC.

that the spectrum does begin to distort at short wavelength). No decay of the FeTPPC signal is observed in the time range studied, implying that cage recombination is fast and steady-state recombination is slow on this time scale. Figure 3a shows the transient spectrum of a pH 10 solution of $(FeTPPC)_2O$ in the presence of 0.1 M TEOA 100 ns after excitation. Figure 3b shows the difference spectrum obtained by subtracting 2 mol of FeTPPC from $(FeTPPC)_2O$. Again, the two spectra virtually overlay. This implies that the transfer of both electrons from the ferryl complex to the TEOA has occurred within 100 ns. Similar results are obtained at pH 8 and if EDTA is used instead of TEOA.

The flash photolysis results not only support the photodisproportionation mechanism but support Mechanism I as the route for the two-electron transfer. While it is generally believed that the first electron transfer from TEOA occurs from the nitrogen, the ferryl complex may instead abstract a hydrogen atom from the α-carbon (similar to the reaction of the ferryl complex with olefins[14] or the ferryl radical cation reaction with alkanes[15]), leading directly to TEOA′ (the combination of steps 6 and 7). This is immediately followed by the second electron transfer from the strong reductant TEOA′. The lack of any detectable pH

Table I. Wavelength Dependence of the Quantum Yield

λ_{excite}	pH	trap	$10^5\phi_0 \pm 10\%$
442	10	TEOA	1.5
409	10, 11	TEOA	5.2
	8, 10, 11	EDTA	5.2
380	10	TEOA	18
	10	EDTA	18
365	10	EDTA	140
350	10	EDTA	270
334	10	EDTA	430
313	10	EDTA	420
290	10	EDTA	430

dependence in the transient spectrum also supports Mechanism I. That this process must be fast is supported by the inability to trap any radical with POBN.

The wavelength dependence of the quantum yield is shown in Table I. It can be seen that the quantum yield increases monotonically with decreasing wavelength down to 334 nm and then flattens out. The most straightforward, though perhaps not the only, interpretation is a charge-transfer excited state (presumably the state at 318 nm).

Since this process appears to be analogous to the trapping of PR_3 by FeO(TPP), a comparison between the quantum yields (see Table I) of these two processes would be valid.

It was anticipated that the quantum yield should increase by going from the noncharged complex $(FeTPP)_2O$ to the tetravalent complex $(FeTPPC)_2O^{4-}$ since Coulombic repulsion in $(FeTPPC)_2O^{4-}$ should help to discourage cage recombination. On the contrary, the quantum yield for $(FeTPPC)_2O$ actually decreases at 409 nm ($\phi_0 = 1 \times 10^{-4}$ for $(FeTPP)_2O$). This may be attributed to two effects, the strength of the solvent cage and ion pairing. Water should form a much stronger cage than benzene owing to hydrogen bonding. This effect probably dominates a Coulombic effect that is limited due to ion pairing, thus giving a lower overall quantum yield. We have attempted to use other solvents that might form less tight cages—CH_3OH, CH_3CH_2OH, $CH_3CH_2OHCH_3$, CH_3COCH_3, and THF—however, substantial formation of monomeric products is detected in both the presence and absence of added NaOH.

Conclusion

A second example of photodisproportionation has been shown. While the goal of this study, an increase in the quantum yield by using a charged complex, was not realized, we have demonstrated that the water-soluble ferryl complex is a strong oxidant capable of oxidizing amines. Further work on charged complexes that are less prone to ion pairing (e.g., tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin) may afford the desired result of a higher quantum yield, by inhibiting cage recombination by Coulombic repulsion.

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Registry No. FeTPPC, 60146-43-2; $(FeTPPC)_2O$, 68033-60-3; EDTA, 60-00-4; TEOA, 102-71-6.

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