we observe the encroachment of intense halogen(π) → Os charge-transfer transitions into the visible region in the case of osmium(III) (Table I), the most dominant spectral feature being an intense band ($\epsilon_{max} \approx 1 \times 10^4$ L mol^{-1} cm^{-1}) at 455 nm in the case of X = Cl and ~590 nm for X = Br. Qualitatively at least, these spectral features seem in reasonable accord with those expected on the basis of a comparison with the spectra of *trans*-$[Os(NH_3)_4X_2]^+$ species,[21-23] for which the corresponding charge-transfer bands are located at much higher energies (270 nm for X = Cl and 320 nm for X = Br). In the case of $[Os(CNR)_4X_2]^+$, the π-accepting RNC ligands should lead to a lowering in the energies of the t_{2g}-type metal orbitals (split, of course, into an orbital doublet and singlet in a field of D_{4h} symmetry) and hence to a decrease in the energy separation between them and the halogen π-type orbitals. The consequence of this is that the $X(\pi) \rightarrow Os(t_{2g})$ transitions shift well into the visible region and impart an intense coloration to these complexes.

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Registry No. *trans*-$Os(CNCMe_3)_4Cl_2$, 88272-01-9; *trans*-$Os(CNCHMe_2)_4Cl_2$, 88272-02-0; *trans*-$Os(CNC_6H_{11})_4Cl_2$, 88272-03-1; *trans*-$Os(CNCMe_3)_4Br_2$, 88272-04-2; *trans*-$Os(CNCHMe_2)_4Br_2$, 88272-05-3; *trans*-$Os(CNC_6H_{11})_4Br_2$, 88272-06-4; *trans*-$[Os(CNCMe_3)_4Cl_2]BF_4$, 88272-08-6; *trans*-$[Os(CNCHMe_2)_4Cl_2]BF_4$, 88272-10-0; *trans*-$[Os(CNC_6H_{11})_4Cl_2]BF_4$, 88272-12-2; *trans*-$[Os(CNCMe_3)_4Br_2]BF_4$, 88272-14-4; *trans*-$[Os(CNCHMe_2)_4Br_2]BF_4$, 88272-16-6; *trans*-$[Os(CNC_6H_{11})_4Br_2]BF_4$, 88272-18-8; $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$, 81282-98-6; $OsO_2Cl_2(PPh_3)_2$, 66984-36-9.

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One-Electron, Visible-Light Photooxidation of Porphyrins in Alkyl Chloride Solutions

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It has been well documented that porphyrin and metalloporphyrin compounds can undergo reversible one-electron oxidation[1-3] to form porphyrin π-cation-radical complexes. These oxidation products have been implicated as intermediates in a number of biological reactions, including heme enzymes,[4,5] photosynthetic reaction centers,[6,7] and photosynthetic model systems,[8] as well as in artificial photocatalytic systems.[9,10] Because of their unusual electronic properties and their novel reactivities, there is great interest in the preparation of these oxidized compounds by chemical, electrochemical, and photochemical methods.[11,12] In particular, the photooxidation of the parent porphyrin by an electron acceptor to give π-cation-radical species has been the subject of many studies.[12-15]

In previous work,[16] we have shown that the diagnostic spectral features that identify specifically whether the porphyrin ring or the metal has been oxidized can be obtained using magnetic circular dichroism (MCD) spectroscopy. Prior to this work, identification of the porphyrin π-cation-radical species in solution was based primarily upon the analysis of optical absorption and ESR spectra.[5,6] In the present paper we report results of the direct photooxidation of porphyrin and metalloporphyrin compounds in alkyl chloride solutions monitored with use of optical absorption and MCD spectra. In these reactions the photooxidation involves a charge-transfer interaction between the photoexcited porphyrin and the alkyl chloride that leads to the formation of a porphyrin π cation radical.

Experimental Section

The 5,10,15,20-tetraphenylporphine (H_2TPP) and metal complexes of the tetraphenylporphine were prepared by literature methods.[17] Reagent grade 1,1,2,2-tetrachloroethane (TCE) obtained from Fisher Chemical Inc. was extracted with several changes of concentrated sulfuric acid followed by alternate washings with water and aqueous sodium hydroxide and then distilled under a nitrogen atmosphere. All other solvents were ACS Certified Spectroanalyzed grade obtained from Fisher Chemical Inc.

Photooxidations of tetraphenylporphine and the magnesium, zinc, cobalt, and copper complexes of tetraphenylporphine were carried out either in dichloromethane solutions containing TCE or CCl_4 or in neat TCE. Nitrogen-saturated solutions were irradiated in a water-cooled cell with visible light (wavelength >400 nm). The light source was a 300-W tungsten-halogen projector lamp, controlled by variable transformer. Quantum yield measurements employing standard ferrioxalate actinometry were carried out with a Jasco CRM-FA spectroirradiator. The porphyrins were dissolved in nitrogen-purged TCE and irradiated in a 1-cm cell at 20 °C with an excitation wavelength of 417 nm. The absorption spectra before and after irradiation were recorded. Initial rates of the photolytic product formation and the quantum yields were determined by monitoring absorption bands in spectral regions where the absorption by the parent porphyrin was negligible (typically about 650 nm). Published molar extinction coefficients were used to determine the concentrations of the porphyrins in solution as follows: H_2TPP, $\lambda = 515$ nm, $\epsilon = 18\,700$;[18] MgTPP, $\lambda = 424$ nm, $\epsilon = 666\,000$;[19] ZnTPP, $\lambda = 419$ nm, $\epsilon = 560\,000$;[20] CoTPP, $\lambda = 527$ nm, $\epsilon = 16\,000$;[21] CuTPP, $\lambda = 540$ nm, $\epsilon = 20\,000$.[21] The degree of photooxidation was easily determined by using the spectrum of a completely oxidized sample. In the case

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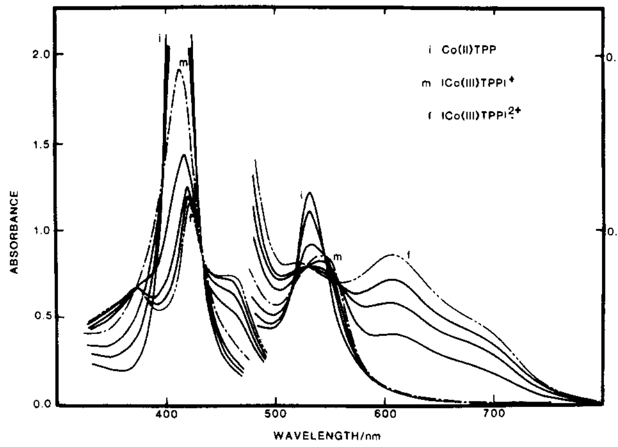

Figure 1. Absorption spectrum changes during the photolysis of (5,10,15,20-tetraphenylporphinato)cobalt(II) in a 1,1,2,2-tetrachloroethane solution with a concentration of 2×10^{-5} mol L^{-1} in a 1-cm cell (i = initial; m = intermediate; f = final). The spectra reflect the photolysis time of 0, 0.5, 2, 3, 4,4.5, 5, and 5.5 min with the tungsten-halogen lamp in a fixed arbitrary position relative to the sample cell.

of the $Co^{II}TPP$ to $[Co^{III}TPP]^+$ conversion, the quantum yield was determined by employing a two-wavelength absorption technique (for $[Co^{III}TPP]^+$, $\lambda = 542$ nm, $\epsilon = 13\,800$).

Absorption spectra were obtained with a Cary 219 spectrophotometer in 10-mm cells. The MCD spectra at room temperature were obtained in 10-mm cells by using a CD spectrophotometer built in this laboratory and a field of 5.5 T from an Oxford Instruments SM2 magnet. The field strength and sign were calibrated by using the negative, visible-region band of aqueous $CoSO_4$, for which a value of $\Delta\epsilon_m = -1.897 \times 10^{-2}$ L mol^{-1} cm^{-1} T^{-1} at 510 nm was calculated. All spectra shown here were automatically digitized as they were recorded, the appropriate baselines were subtracted, and the resulting spectra were replotted with a computer.

Results and Discussion

The absorption and MCD spectra of the unoxidized CoTPP in CH_2Cl_2, shown in Figures 1 and 2, are qualitatively similar to previously reported data.[22] The absorption spectrum is characterized by a strong Q_{0-1} band at 527 nm, which completely obscures the very weak Q_{0-0} component, and an intense B band at 411 nm. In the MCD spectrum, intense *A* terms characteristic of an unoxidized porphyrin are associated with the Q_{0-1} and B bands; a weak *A* term at 585 nm is also observed, which serves to identify the location of the Q_{0-0} band. Irradiation of $Co^{II}TPP$ with a wavelength >400 nm in the presence of TCE results in changes in the absorption specrum (Figure 1) that are characterized by isosbestic points at 543, 515, 432, and 399 nm in the initial period of photolysis and at 556, 530, 433, and 374 nm following prolonged irradiation. The MCD spectrum of the parent $Co^{II}TPP$ in CH_2Cl_2 and the MCD spectra of the species produced at the completion of each of the two stages of the photolysis, which correspond to the absorption spectra i (initial), m (intermediate), and f (final) in Figure 1, respectively, are shown in Figure 2. The analysis of all these spectral changes indicates that the clean photooxidation of $Co^{II}TPP$ to $[Co^{III}TPP]^+$ is followed by oxidation to $[Co^{III}TPP]^{2+}$, which is a π-cation-radical complex. This assignment can be inferred from the known optical absorption spectra of the parent $Co^{II}TPP$ and the one- and two-electron-oxidation products, and is clearly confirmed by the MCD spectra of the three species shown in Figure 2. There are also distinct changes in the MCD spectrum when $Co^{II}TPP$ is oxidized to $[Co^{III}TPP]^+$. The absorption spectrum of $[Co^{III}TPP]^+$ is characterized by a strong Q_{0-0} band at 542 nm, a weak Q_{vib} band at 510 nm, and a B band at 405 nm of reduced intensity, each of which exhibits an *A* term in the MCD spectrum. The nature of such oxidized species is a matter of some controversy since the stable oxidized product can be formed either from metal-based orbitals or from the porphyrin π system. The oxidation of $Co^{II}TPP$ to the monocation was originally formulated as a metal-based oxidation.[23] Recent investigations, however, have suggested that the one-electron oxidation of $Co^{II}TPP$ involves the porphyrin π system, forming a $[Co^{II}TPP]^{+\cdot}$ π-cation-radical species.[24] The distinct MCD *A* terms observed in our spectrum of this oxidized species clearly discriminate between metal and porphyrin π-ring oxidation products and indicate that the one-electron-oxidized product of these $Co^{II}TPP$ solutions is better described as $[Co^{III}TPP]^+$, a metal-oxidized species.

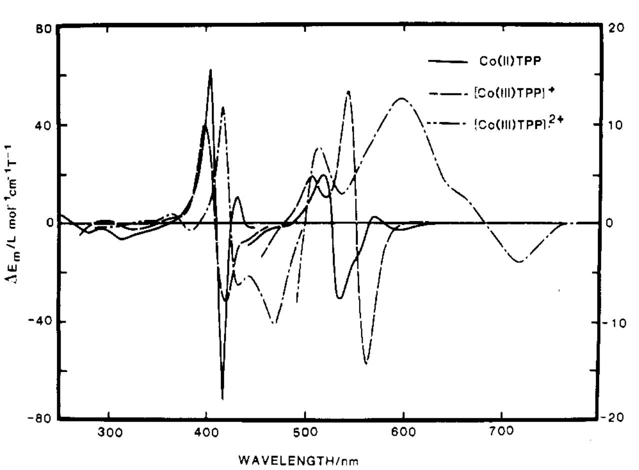

Figure 2. MCD spectra of (5,10,15,20-tetraphenylporphinato)cobalt(II) in CH_2Cl_2 and of the (5,10,15,20-tetraphenylporphinato)-cobalt(III) cation and the (5,10,15,20-tetraphenylporphinato)cobalt(III) π cation radical in a 1,1,2,2-tetrachloroethane solution at room temperature.

Photooxidation of $[Co^{III}TPP]^+$ results in the formation of $[Co^{III}TPP]^{2+\cdot}$. The assignment as a porphyrin π-cation-radical species is based upon a comparison of the MCD spectrum of this species with the MCD spectra of other, well-known porphyrin π-cation-radical species.[16] There are dramatic changes in the absorption and the MCD spectra when $[Co^{III}TPP]^+$ is oxidized to $[Co^{III}TPP]^{2+\cdot}$. This π-cation-radical species has an absorption spectrum characterized by an overlapping series of bands through the visible region, while in the B-band region the most intense band is centered at 420 nm. The MCD spectrum in the visible region has a negative MCD *B* term, at about 700 nm, and a series of positive bands between 500 and 650 nm that are characteristic of a π-electron oxidation. These features, together with an apparent Faraday *A* term under the B (Soret) band in the 400-nm region of the spectrum, appear to be diagnostic for A_{2u} porphyrin π-cation-radical complexes.[16] Similar MCD spectra are also observed when MgTPP and ZnTPP are irradiated in the presence of an excess of TCE or CCl_4 in a solution of dichloromethane.[25] Irradiation of rigorously deoxygenated, neat dichloromethane solutions of many metal complexes of tetraphenylporphine, and specifically of MgTPP and ZnTPP,

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[25] ESR measurements, along with the optical and MCD data, provide evidence to show the presence of the π-cation-radical species in the photolyzed alkyl chloride solutions. When the nitrogen-purged solutions of ZnTPP in TCE were irradiated in situ in the ESR cavity with visible light (wavelength >420 nm), a stable ESR signal appeared, which was identical with that reported for a $(ZnTPP^+ \cdot Cl^-$ species produced electrochemically.[6] Similar ESR results were obtained for MgTPP.

Table I. Quantum Yields and Energetics for the Photooxidation of Tetraphenylporphine and Metallo Complexes of Tetraphenylporphine in a 1,1,2,2-Tetrachloroethane Solution Using an Excitation Wavelength of 417 nm

porphyrin	quantum yield	$E(P^+/P)$,[a] V (SCE)	$E(T)$,[b] eV	$E(P^+/P^T)$,[c] V (SCE)
MgTPP	0.79	0.54	1.48	−0.96
ZnTPP	0.16	0.71	1.59	−0.88
H_2TPP	0.002[d]	0.95	1.43	−0.48
$Co^{II}TPP$	0.019	0.32		
$[Co^{III}TPP]^+$	0.012	0.74		
CuTPP	<0.0001	0.90	1.66[e]	−0.76

[a] The electrochemical data reported for oxidation in CH_2Cl_2.[11] [b] Lowest triplet-state energy.[10] [c] Triplet-excited-state redox potential. [d] Oxidation performed in TCE containing 1% pyridine (v/v).[32] [e] Short-lived triplet state.

using visible light, however, does not result in any spectral change in the UV–visible spectra.

The spectral results presented above and the quantum yields of the porphyrin photooxidation in a TCE solution (Table I), which were measured by using monochromatic excitation light at 417 nm, are consistent with the simple scheme

$$\mathrm{MTPP} \xrightarrow{h\nu} \mathrm{MTPP}^*$$

$$\mathrm{MTPP}^* + \mathrm{RCl} \rightarrow \mathrm{MTPP}^{+\cdot} + \mathrm{R}\cdot + \mathrm{Cl}^-$$

where MTPP* is the porphyrin in an electronically excited state and RCl is the alkyl chloride. Generally, for the alkyl chloride compound to be capable of oxidizing a porphyrin from its excited state, it should exhibit, on thermodynamic grounds, a high redox potential (cf. Table I). The alkyl chloride oxidants used here, CCl_4 and TCE, seem to fulfill these requirements, since a redox potential of −0.78 V (vs. SCE) has been reported for CCl_4[26] and the value of −0.9 V can be estimated for TCE.[27] The fate of the alkyl chloride radicals, R·, evolved in the oxidation reaction can be predicted from the results of electrochemical reduction of alkyl halides and radiolytic studies.[28,29] The $CCl_3\cdot$ radicals undergo rapid dimerization reactions ($k \sim 10^8$–10^9 L mol^{-1} s^{-1} [30]). The decay of alkyl radicals containing vicinal halide substituents, like $CHCl_2CHCl\cdot$, can lead to the formation of alkene derivatives through the elimination of halides.[31]

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Registry No. $Co^{II}TPP$, 14172-90-8; $[Co^{III}TPP]^{2+\cdot}$, 38414-01-6; $[Co^{III}TPP]^+$, 28132-69-6; ZnTPP, 14074-80-7; CuTPP, 14172-91-9; MgTPP, 14640-21-2; H_2TPP, 917-23-7; CCl_4, 56-23-5; CH_2Cl_2, 75-09-2; TCE, 79-34-5.

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