Offprint from
Optical Properties and Structure of Tetrapyrroles
Editors: G. Blauer, H. Sund

EXCITED STATE ELECTRON TRANSFER OF CARBONYL[MESOTETRA(P-TOLYL) PORPHYRINATO]OSMIUM(II) COMPLEXES. ONE AND TWO ELECTRON PHOTO-REDOX PROCESSES.

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Introduction

Naturally occuring iron porphyrin complexes (hemochromes) are well known to be photosensitive or to participate in light-driven reactions. The photodissociation of CO from carbonyl hemoglobin and related compounds has been studied extensively. In order to identify the reactive excited state we investigated an analogous ruthenium complex.(1) The substitution of Fe(II) by the homologous Ru(II) modifies the electronic structure of the metalloporphyrin in a well-defined way. The study of the photochemical and photophysical properties of the ruthenium compound contributed thus to a better understanding of the photochemistry of carbonyl hemoglobin. The present work is an extension of this investigation. Iron or ruthenium is replaced by osmium the heaviest member of the homologous group of metals.

Other hemochromes such as the cytochromes participate in light-induced electron transfer reactions of the photosynthesis. Although the photoredox behavior of some iron porphyrins was studied(2-5), the investigation of these compounds is generally hampered by their kinetic lability. For this reason the corresponding osmium porphyrins ("osmochromes"), which are substitutionally inert, were suggested to serve as models for hemochromes.(6) Hence we expected that the study of the photoredox behavior of osmochromes would shed some light on corresponding reactions of cytochromes. In this regard it is important that many Fe(II) and Os(II) complexes may be oxidized at comparable potentials while Ru(II) requires higher potentials.(6,7) Excited state electron transfer reactions of ruthenium porphyrins were already investigated.(8,9)

A further important aspect of the present work is related to the growing interest in metalloporphyrins as attractive candidates for photosensitizers in artifical photosynthesis.(10) In such systems excited metalloporphyrins undergo one-electron transfer as primary photoreaction. In subsequent processes these one-electron redox reactions must be coupled by catalysts such as metallic platinum because photochemical water splitting or other useful photoreactions require multi-electron transfer steps. These systems could possibly be simplified if the excited metalloporphyrin would itself participate in multi-electron redox reactions. For this purpose osmium porphyrins are a good choice. Not only the oxidation states II and III but also IV and VI of osmium in porphyrin complexes are stable and spectroscopically well characterized.(6,11-13) While the photophysics of some osmium porphyrins was investigated extensively(12,13), only a few, mostly qualitative observations of the photochemistry of these compounds were reported.(14-17) The present study adds new important data and thus gives a rather complete picture of the photoreactivity of these compounds.

Results

Electronic Spectra

The electronic spectra of [Os(TTP)(CO)L] with TTP = mesotetra-(p-tolyl)porphyrin and L = methanol or pyridine are very similar.(17,18) In the absorption spectrum (Fig. 1) of [Os(TTP)(CO)(CH_3OH)] (*1*) the Soret band appears at λ_{max} = 411 nm (log ε = 5.35) while the β band occurs at λ_{max} = 523 nm (log ε = 4.21). The α band shows up as a shoulder at λ = 555 nm (log ε = 3.55). Two low-intensity bands appear at λ_{max} = 593 nm (log ε = 3.33) and 645 nm (log ε = 2.72; shoulder). The corresponding absorption bands of [Os(TTP)(CO)(pyridine)] (*2*) in CH_2Cl_2 occur at λ_{max} = 412 nm (log ε = 5.48), 522 nm (log ε = 4.25), 560 nm (log ε = 3.69), 591 nm (log ε = 3.53) and 651 nm (log ε = 3.02).

Both compounds show a photoluminescence at λ_{max} = 653 nm for *1*

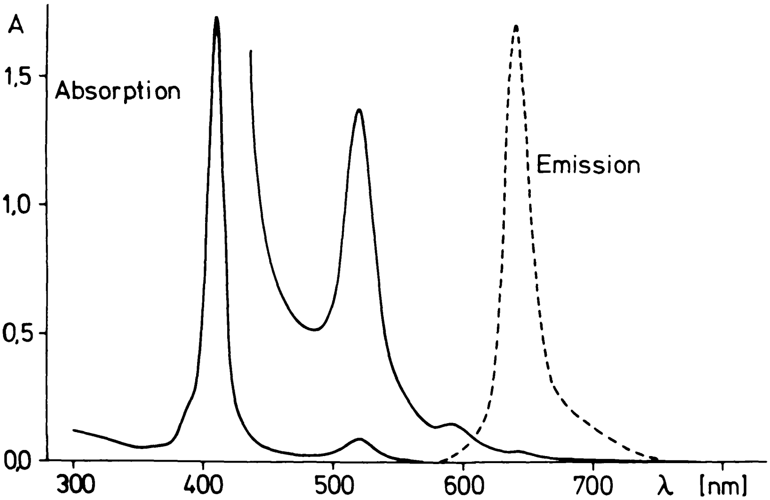

Fig. 1: Electronic spectra of *1* in CH_2Cl_2. Absorption (——): 7.8×10^{-6} M (8.5×10^{-5} M for long-wavelength region) solution, 1-cm cell. Emission (----): Intensity in arbitrary units, not corrected; λ_{exc} = 546 nm.

(Fig. 1) and 651 nm for *2* (not corrected for photomultiplier response) at room temperature and in a variety of solvents such as CH_2Cl_2 and at different exciting wavelengths (365, 405 and 546 nm). The emission of *1* decays with a first-order rate constant of $k = 1.1\times10^{8}\ s^{-1}$. By comparison with the integrated emission intensity of europium thenoyltrifluoroacetonate (ϕ = 0.56 in acetone)(19) at $\lambda_{exc.} = 366$ nm the emission quantum yield of *1* was estimated to be $\phi = 4\times10^{-3}$. The emission was hardly quenched by oxygen.

Photosubstitution. The complexes *1* and *2* do not undergo any efficient photosubstitution of the axial carbonyl ligand upon long-wavelength irradiation ($\lambda_{irr} > 390$ nm). The spectrum of *2* dissolved in pyridine changed to that of $Os(TTP)(pyridine)_2$ (16,17) upon irradiation of the β or Soret band of *2* only after very long irradiation times. The quantum yield of CO substitution was estimated to be $\phi < 3\times10^{-7}$ ($\lambda_{irr} = 405$ nm).

Luminescence Quenching. Several electron donors and acceptors were observed to quench the emission of *1* and *2* in solution at room temperature. However, in some cases additon of the quencher resulted in changes of the absorption spectra of *1* and *2*, indicating ground state interaction or a chemical reaction. Two compounds, N,N-dimethylaniline (DMA) and p-nitrobenzaldehyde (NBA), did not affect the absorption spectra of the osmium porphyrins but quenched the emission according to a Stern-Volmer kinetics. For *1* in CH_2Cl_2 ($\lambda_{irr} = 546$ nm) the slopes of the Stern-Volmer plots were $Ksv = 439\ M^{-1}$ (DMA) and $Ksv = 378\ M^{-1}$ (NBA). From the lifetime of *1* ($\tau = 9.4\times 10^{-9}\ s^{-1}$) the quenching constants $k_q = 4.7\times10^{10}\ mol^{-1}s^{-1}$ (DMA) and $k_q = 4.0\times10^{10}\ mol^{-1}s^{-1}$ (NBA) were obtained. Continuous irradiation of *1* in the presence of the quenchers did not lead to any permanent chemical change. The quenching was thus associated with a reversible process.

Relative quantum yields of emission of *1* were determined in two different solvents (CH_2Cl_2 and CCl_4) at two different exciting wavelengths (365 and 520 nm). At 520 nm (β-band) the integrated emission intensities were equal in both solvents. At 365 nm (Soret band) the emission efficiency in CCl_4 was only 0.77 of that obtained in CH_2Cl_2.

Photooxidation. In solutions of chlorocarbons such as CH_2Cl_2, $CHCl_3$ or CCl_4 the complexes *1* and *2* underwent an irreversible photochemical reaction upon irradiation with light of $\lambda >$ 300 nm. Typical spectral changes which accompanied the photolysis are shown for *2* in Fig. 2. Clear isosbestic points were observed up to about 80 % conversion. Later, secondary photolysis obscured the spectral changes. The nature of the photoproduct did apparently not depend on the ligand L. The product is characterized by the following absorption bands: λ_{max} = 395, log ε = 4,70; λ_{max} = 442 nm (shoulder); λ_{max} = 503, log ε = 4,02; λ_{max} = 584, log ε = 3.85; λ_{max} = 610 nm (shoulder). Although the photoproduct could not be identified definitely, it

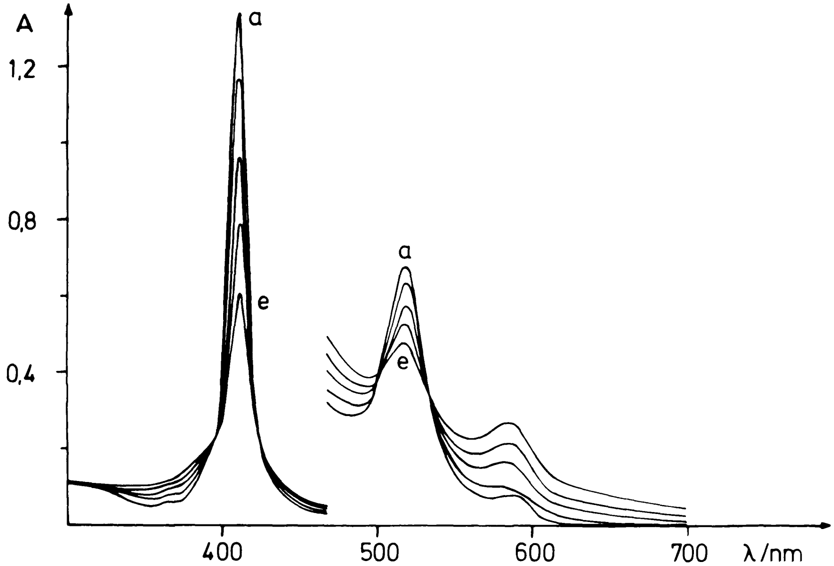

Fig. 2: Spectral changes during the photolysis of 4.4×10^{-6} M *2* in CCl_4 at (a) 0 and (e) 13-min irradiation time, λ_{irr}>420 nm, 1-cm cell; absorbance × 0.1 for long-wavelength region.

is assumed to be [Os(IV)(TTP)Cl_2]. This is supported by several arguments. Many transition metal complexes were observed to be photooxidized in chlorocarbon solvents.(20,21) Most compounds undergo one-electron oxidations. Two-electron oxidations occur if the metal exists in a stable oxidation state which is higher by two units.(22) This is certainly true for Os(II) which may not only be oxidized to Os(III) but also to Os(IV). Indeed, Os(II)(octaethylporphyrin)$[P(OCH_3)_3]_2$ was observed to be photooxidized to Os(IV)(octaethylporphyrin)Cl_2.(15) Nevertheless, an Os(III) porphyrin must be considered to be a reasonable alternative as final photoproduct. However, the oxidation of Os(II) to Os(III) is usually not associated with large spectral changes in contrast to those observed during the photooxidation. The absorption spectra of Os porphyrins with the metal in higher oxidation states (IV and VI) are characterized by the appearance of longer-wavelength (λ > 600 nm) absorption bands,which are due to the occurance of low-energy charge transfer (CT) transitions (12), in agreement with our observation. If the photooxidation produces Os(III) porphyrins the complexes $[Os(TTP)(CO)L]^+$ or [Os(TTP)LCl] would be reasonable candidates. $[Os(TTP)(CO)L]^+$ can be excluded because it should easily be reduced back to [Os(TTP)(CO)L]. This was not observed. The spectrum of [Os(TTP)ClL] should depend on L to some degree. Again, the photoproduct was apparently the same regardless wether L was methanol or pyridine.

Quantum yields of photooxidation were dependent on the irradiating wavelength and the chlorocarbon solvent. For *1* the following efficiencies were obtained: λ_{irr} = 333 nm, ϕ = 0.35 in CCl_4 (0.034 in CH_2Cl_2); λ_{irr} = 365 nm, ϕ = 0.045 (0.005); λ_{irr} = 405, ϕ = 0.039 ($\sim$ 0); λ_{irr} = 546 nm, ϕ < 0.001 ($\sim$ 0).

Discussion

The electronic spectra of *1* and *2* show only $\pi\pi^*$ bands of the porphyrin ligand (Fig. 1). The B(0,0) or Soret bands appear at

24 330 cm^{-1} (*1*) and 24 270 cm^{-1} (*2*). Q bands occur at 19 120 cm^{-1} (0,1 or β) and 18 020 cm^{-1} (0,0 or α) for *1* and 19 160 cm^{-1} (0,1 or β) and 17 860 cm^{-1} (0,0 or α) for *2*. Most remarkable are the longer-wavelength absorption bands of lower intensities which we assign to vibrational levels of the T_1 ($\pi\pi^*$) state. These bands appear at 16 860 cm^{-1} (0,1) and 15 500 cm^{-1} (0,0) for *1* and 16920 cm^{-1} (0,1) and 15 360 (0,0) for *2*. To our knowledge this seems to be the first case where spin-forbidden $\pi\pi^*$ transition of a porphyrin are identified in absorption. The third-row transition metal osmium induces apparently enough singlet-triplet mixing by spin-orbit coupling ("heavy atom effect") in the porphyrin. As a consequence the spin selection rule breaks down partially. Several arguements support this assumption.

The emission of *1* (Fig 1) at 15 310 cm^{-1} and *2* at 15 630 cm^{-1} is certainly the $\pi\pi^*$ phosphorescence from the T_1 (0,0) state of the porphyrin. The energy separation between the Q (0,0) and the T_1 (0,0) absorption band ($\Delta E \sim 2500$ cm^{-1}) is similar to that observed for other metalloporphyrins.(12,23) In agreement with a strong spin-orbit coupling the lifetime of the T_1 state is extremely short ($\tau \sim 10^{-8}$ s for *1*). For this reason *1* and *2* show a relatively intense phosphorescence even at room temperature and in solution which is hardly quenched by oxygen.

The emission maxima of *1* and *2* are almost resonant with the longest energy absorption maxima (the luminescence spectra are not corrected; the real emission maxima should appear at lower energies). In absorption and emission these maxima are thus assigned to the singlet-triplet $\pi\pi^*$ (0,0) transitions. Light absorption into this long-wavelength band by the 632 nm line of a He/Ne laser is indeed associated with this emission. This observation excludes the possibility that this absorption is due to an impurity or is caused by another electronic transition which occurs at lower energies than the $\pi\pi^*$ transitions.

The assignment of the $\pi\pi^*$ T_1 (0,1)bands of *1* and *2* is certainly also reasonable. The energy gap between the (0,0) and (0,1) Q (ΔE = 1100 cm^{-1}) and T_1 (ΔE = 1360 cm^{-1}) bands of *1* are comparable. The corresponding values of *2* are ΔE = 1300 cm^{-1} and 1560 cm^{-1}. (The Q (0,0) band was not exactly located, see Fig. 1.) In this context it is remarkable that in contrast to our observation the lowest excited state of the corresponding octaethylporphyrin (OEP) complex [Os(OEP)(CO)(pyridine)] is not the T_1 ($\pi\pi^*$) but a CT (Os to porphyrin) transition.(12)

Photochemistry

Photosubstitution. In analogy to similar M(CO)(porphyrin) complexes with M = Fe and Ru (1) the compounds *1* and *2* may be expected to undergo a photodissociation/substitution according to (S = coordinating solvent):

$$[Os(TTP)(CO)L] \xrightarrow{h\nu} [Os(TTP)L] + CO$$

$$[Os(TTP)L] + S \rightarrow [Os(TTP)LS]$$

It has been reported that this reaction indeed occurs.(14,16, 17). However, it is rather inefficient at least for long-wavelength irradiation ($\lambda > 390$ nm). The photolysis of *2* in pyridine produced $Os(TTP)(pyridine)_2$ with a quantum yield $\phi < 3\times10^{-7}$. This observation is not surprising. In the case of iron carbonyl porphyrins such as carbonyl hemoglobin an efficient photolysis occurs ($\phi \sim 1$) because the reactive ligand field (LF) excited state, which is the lowest-energy excited state of these iron porphyrins, is effectively populated from $\pi\pi^*$ states.(1) If Fe is replaced by Ru the energy of the lowest LF state is raised slightly above the lowest $\pi\pi^*$ state of the porphyrin ligand. This leads to a considerable drop of the photosubstitution quantum yield because the most efficient deactivation path is now the radiative (phosphorescence) and radiationless transition from $T_1(\pi\pi^*)$ to the ground state.(1)

Since osmium as a third-row transition metal has the largest LF splitting of the homologous metals the energy of the reactive LF state increases again. Excited state deactivation occurs now almost exclusively via the T_1 ($\pi\pi^*$) state by phosphorescence and radiationless transition to the ground state.

Phosphorescence Quenching by Electron Transfer. The first reduction potentials of *1* and *2* were reported to be $E_{1/2}$ = +0.71 V and +0.68 V vs. SCE.(6,17) Taking into account the energy of the emitting T_1 ($\pi\pi^*$) states (0,0 band of *1* at 15 500 cm^{-1} or 1.92 V and of *2* at 15 360 cm^{-1} or 1.90 V) they should be oxidized at $E_{1/2}$ = -1.21 V and -1.22 V. Accordingly the T_1 ($\pi\pi^*$) state should be susceptible to a variety of electron transfer reactions in solution. However, only very fast, essentially diffusion-controlled redox reactions can occur due to the very short life time of T_1 ($\tau \sim 10^{-8}$ s for *1*). This expectation was confirmed. Obeying a Stern-Volmer kinetics the phosphorescence of *1* in CH_2Cl_2 was quenched oxidatively by NBA ($E_{1/2}$ = -0.86 V vs. SCE) with a second order rate constant of $k_q = 4.0\times10^{10}$ $mol^{-1}s^{-1}$. Reductive quenching of *1* ($k_q = 3.7\times10^{10}$ $mol^{-1}s^{-1}$) was observed with DMA ($E_{1/2}$ = +0.78 V). Although the first oxidation potential of *1* (or *2*) is not known it should occur at potentials less negative than approximately -1.1 V according to this observation. Oxidative and reductive quenching takes apparently place by reversible electron transfer, since it was not associated with any permanent chemical change. This quenching can not occur by an energy transfer mechanism because these quenchers do not possess low-energy excited states.

Photooxidation

Many transition metal complexes are photooxidized in halocarbon solvents.(20,21) In most cases the metal complexes undergo one-electron oxidations. Two-electron oxidations of the metals are favored if higher oxidation states are stable and accessible at moderate potentials. This was observed for Pt(II)(bipyridyl) Cl_2 which undergoes a light induced oxidative addition in chlorcarbon solvents such as $CHCl_3$. Pt(IV)(bipyridyl)Cl_4 is obtained as stable product.(22) Higher oxidation states such as IV and VI are also stable and well known for osmium porphyrins.(6, 12,17) It is thus suggested that the photolysis of *1* or *2* in chlorocarbon solvents e.g. CCl_4 proceeds according to the following reaction sequence:

$$[Os(TTP)(CO)L] + CCl_4 \xrightarrow{h\nu} [Os(TTP)(CO)L]^+Cl^- + \cdot CCl_3$$

$$[Os(TTP)(CO)L]^+Cl^- + \cdot CCl_3 \longrightarrow [Os(TTP)Cl_2] + CCl_2 + CO + L$$

An internally excited state of *1* or *2* undergoes an one-electron transfer to the solvent in the primary photochemical step. The chloromethyl radicals such as $\cdot CCl_3$ are strong one-electron oxidants. Consequently, the oxidized osmium porphyrin obtained in the primary step is further oxidized in a subsequent second electron transfer to yield Os(TTP)Cl_2 as final product. The two-electron reduction of CCl_4 leads to the release of two chloride ions, which are attached to the osmium as ligands, and the generation of the carbene CCl_2.

Generally, excited state electron transfer requires a long-lived excited state because the excited molecule has to wait for a diffusional encounter with an electron donor or acceptor.(9) Usually only the lowest-energy excited state meets this requirement. This applies also to the phosphorescence quenching of *1* by DMA and NBA. However,the photooxidation of *1* or *2* in chlorocarbon solvents is efficient only upon irradiation of the shorter-wavelength absorption bands. This means that higher excited states of the complexes are involved in the initial electron transfer step. This seems to be surprising because of the very short lifetime of higher excited states. However, long lifetimes are apparently not required because the complex is already in close contact with the solvent molecules as acceptors prior to excitation.

The formation of the primary one-electron redox products is assumed to be preceded by the population of a charge-transfer-to-solvent (CTTS) excited state from an internal excited state of the complex.(20) The energy of this CTTS state depends on the reduction potential of the complex and the oxidation potential of the chlorocarbon solvent. If CH_2Cl_2 is replaced by CCl_4 the CTTS state is shifted to lower energies because CCl_4 ($E_{1/2}$ = -0.78 V) is a stronger oxidant than CH_2Cl_2 ($E_{1/2}$ = -2.33 V).(21) Consequently, higher internal excited states of the complex are required to populate the reactive CTTS state if CCl_4 is replaced by CH_2Cl_2 in agreement with our observation. For the photooxidation of *1* the light-sensitive wavelength region is blue-shifted when CH_2Cl_2 is used as solvent instead of CCl_4. These considerations apply also to the wavelength dependence of the quantum yield of phosphorescence of *1*. Since the energy of the Q ($\pi\pi^*$) state ($\lambda_{exc.}$ = 546 nm) is not sufficient to populate the CTTS state in CH_2Cl_2 or CCl_4, the phosphorescence intensity is the same in both solvents. However, the emission yield decreases in CCl_4 compared with CH_2Cl_2 if the B ($\pi\pi^*$) is excited ($\lambda_{exc.}$ = 405 nm). In CCl_4 the radiationless deactivation from the B state to the emitting $\pi\pi^*$ triplet competes apparently with the population of the reactive CTTS state. In CH_2Cl_2 the CTTS state seems to be at much higher energies. It can not be populated any more efficiently from the B state of *1*.

Acknowledgment. Financial support for this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We are grateful to Dr. K. Oesten for providing samples of the osmium porphyrin complexes.

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Received July 13, 1984

Discussion

Fuhrhop: How do you explain the formation of a molecular complex between a positively charged central ion in porphyrins and a positively charged pyrazinium ligand? Are there other examples?

Vogler: The coordination of a positively charged ligand to a metal cation is by no means rare in coordination chemistry. Ligands such as the nitrosyl cation (NO^+), diazonium cations ($N \equiv N^+$-R), and carbyne cations (C^+-R) are well-documented examples.

Gouterman: Do you get CO loss from Os(TTP)CO(L) when you pump into the Soret band? The S_2 state may live some picoseconds and can then lead to ligand field states.

Vogler: This is exactly the process which in our opinion is responsible for the photosubstitution of CO upon irradiation into the Soret band.

Eilfeld: Were you able to trap the dichlorocarbene formed in the course of photolysis of [O_S(TTP)(Co)L], e.g. by cyclo-additions?

Vogler: We did not do this in this work. However, chlorocarbenes are well known to insert readily in carbon-halogen bonds. In a related case (photooxidation of Pt(dipyridyl)Cl_2 in $CHCl_3$; see ref. 22 of our paper) we were able to detect the insertion product ($CHCl + CHCl_3 \longrightarrow CHCl_2\text{-}CHCl_2$).

Buchler: You mentioned that in the oxidized iron tetrabenzporphyrin carbonyl pyridine radical cation [Fe^{II}(TBP)COPy]$^+$ the CO stretching frequency is 2020 cm^{-1} while it appears at 1975 cm^{-1} in the neutral Fe^{II}(TBP) COPy. This increase in frequency indicates a destabilisation of the CO bond to Fe^{II} only if the correction for the increase in charge according the rules of Ibers et al. has already been applied.

Vogler: You are correct. But this problem does not interfere with my argument. We only wanted to show that the removal of a porphyrin π-electron does not lead to a loss of the CO ligand.

Myer: Have you studied the dissociation profiles? The Soret band has shoulders on both the high and low wavelength side. The dissociation profile will help in determining what transition is involved.

Vogler: The efficiency of dissociation was so low that we could only determine an upper limit of the quantum yield in the Soret region. For this reason, wavelength-dependent measurements were not carried out.