

finding¹ that the P-backbonding interaction involves the phosphorus p orbitals to a greater extent than the d orbitals does not survive improvements in the atomic basis set. Although the total back-bonding populations do increase with electronegative substitution, the increase in d orbital population at phosphorus upon oxidation is found to be very nearly constant.

Multiconfiguration SCF potential energy surfaces for the dissociation of oxygen from some of the excited electronic states of phosphine oxide were presented. The majority of these states are found to be repulsive, although a small potential bump is present in one of the higher singlet levels and one triplet state has a bound potential leading to ions. The states are best described as transitions from nonbonding oxygen lone pair orbitals to a phosphorus a_1 Rydberg orbital. MCSCF optimization of the lowest vertical states, for which the upper orbital was of e (that is π) symmetry, showed that this π orbital possessed Rydberg character, rather than being a p_π - d_π antibonding orbital as implied by the triply bound resonance structure. This finding may be modified with the use of the largest basis set, and electronegative substituents at the phosphorus are likely to increase the π valence character of the excited orbital. At higher excitation energies, electrons may be excited from the PO dative σ bond into phosphorus Rydberg levels. The excited states can be rationalized entirely in terms of a singly bound resonance structure for the ground state.

Calculations on the thiophosphoryl bond show that it is weaker than the PO bond. The relative importance of the triply bound resonance structure in phosphine sulfide is less than in the oxide. Otherwise, the bonding picture largely resembles that of the phosphine oxides. Electronegative substitution acts to increase the PS bond strength, just as for the phosphoryl bond itself. d orbitals on sulfur play little role in the dative sulfide bonding.

A paper comparing the phosphoryl and thiophosphoryl bonds to valence isoelectronic molecules such as the singly bound H_3SiF and triply bound H_3SN will appear shortly.⁴¹

Acknowledgment. We thank Kenneth Dykema for providing the structure of silyl phosphine in advance of publication and the North Dakota State University Computer Center for computer time. This work was supported by AFOSR Grant 82-0190.

Registry No. H_3PO , 13840-40-9; PH_3 , 7803-51-2; $P(CH_3)_2$, 593-54-4; $P(NH_2)_2$, 13598-67-9; $P(OH)_2$, 25756-87-0; PFH_2 , 14500-81-3; PF_2H , 14984-74-8; PF_3 , 7783-55-3; $P(SiH_3)_2$, 14616-47-8; $P(PH_2)_2$, 13445-50-6; $P(SH)_2$, 13965-74-7; $PC(H)_2$, 14500-83-5; $H_2(CH_3)PO$, 7187-92-0; $H_2(NH_2)PO$, 14616-26-3; $H_2(OH)PO$, 6303-21-5; H_2FPO , 14616-32-1; HF_2PO , 14939-34-5; F_3PO , 13478-20-1; $H_2(SiH_3)PO$, 95123-24-3; $H_2(PH_2)PO$, 68570-63-8; $H_2(SH)PO$, 14056-58-7; H_2ClPO , 14616-31-0; $(OPH_2)_2$, 73416-76-9; H_3PS , 35280-73-0.

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Picosecond Studies of Ruthenium(II) and Ruthenium(III) Porphyrin Photophysics

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Abstract: We report the results of picosecond and slower time scale transient absorption and emission measurements on a series of ruthenium(II) and ruthenium(III) octaethylporphyrins ($Ru(OEP)(L_1)(L_2)$). The ruthenium(II) porphyrins are of three types. First are the carbonyl complexes in which $L_1 = CO$ and $L_2 = EtOH$, pyridine (py), or 1-methylimidazole (1-MeIm), which all exhibit similar spectral and kinetic behavior. The lowest excited states of these molecules are assigned as the ring $^3T(\pi, \pi^*)$ in agreement with previous work on similar complexes. The $^3T(\pi, \pi^*)$ state has a lifetime of $\sim 75 \mu s$ at room temperature in degassed solution, as measured by decay of phosphorescence emission at 657 nm or relaxation of absorption changes induced by a 10-ns laser flash. Absorption difference spectra obtained upon excitation with a 35-ps flash do not decay over a 6-ns time scale, in agreement with the slower measurements. The spectra exhibit bleaching in the ground-state bands and the appearance of two new transient absorption peaks ($\log \epsilon \sim 3.7$) near 720 and 815 nm; these features are consistent with the assignment of the transient as a metalloporphyrin (π, π^*) triplet. The $^1Q(\pi, \pi^*)$ lifetimes in these carbonyl complexes appear to be < 35 ps. Different photophysical behavior is observed for $Ru^{II}(OEP)(P-n-Bu_3)_2$. We assign the lowest excited state of this complex as a ($d_\pi, e_g(\pi^*)$) metal-to-ring charge transfer (CT) state. The lifetime of this transient is 12 ± 3 ns, as measured by decay of the absorption changes in toluene following picosecond excitation. The absorption difference spectrum contains a distinct new absorption peak near 710 nm, which is expected for a (d, π^*) CT excited state on the basis of resemblances with ground-state spectra of metalloporphyrin π -anion radicals. The absorption changes observed upon excitation of $Ru^{II}(OEP)(NO)(OMe)$ in toluene with a 35-ps flash decay in two steps, with lifetimes of ≤ 50 ps and > 5 ns. These components are tentatively assigned to relaxation of the ring $^1Q(\pi, \pi^*)$ and $^3T(\pi, \pi^*)$ excited states. The triplet decay may proceed via ring $(\pi) \rightarrow [metal d_\pi + NO(\pi^*)]$ CT states predicted to be in the proper energy range from previous theoretical work. Finally, excited $Ru^{III}(OEP)(P-n-Bu_3)(Br)$ decays completely in ≤ 35 ps, possibly via a (π, d_π) ring-to-metal CT excited state. Our results are discussed in terms of recent absorption and emission measurements and calculations on d^6 metalloporphyrins and are compared to previous picosecond measurements on analogous osmium(II) porphyrins.

Recent absorption and emission studies and iterative extended Hückel (IEH) calculations have been performed on a number of Fe^{II} , Ru^{II} , and Os^{II} porphyrins.^{1,2} These investigations have shown that the electronic properties of these complexes are strongly

affected by the σ -donating and π -accepting nature of axial ligands. The relative energies of the lowest ring (π, π^*) and metal-to-ring ($d_\pi, e_g(\pi^*)$) charge-transfer (CT) excited states appear to be of major importance in governing the photophysical behavior. A

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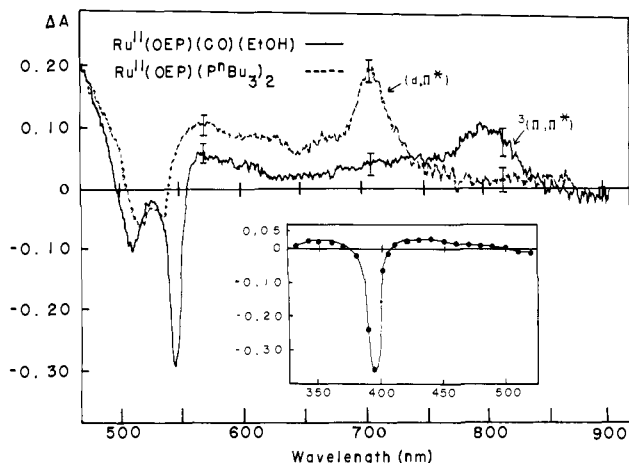


Figure 1. Excited-state absorption difference spectra observed at a 215-ps time delay following excitation with 35-ps, 355-nm flashes. The solid spectrum (—) is for $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{EtOH})$ in ethanol (100 μM , 2 mm path). Similar spectra were obtained in toluene when EtOH was replaced by py or 1-Melm. The dashed spectrum (---) is for $\text{Ru}^{\text{II}}(\text{OEP})(\text{P}-n\text{-Bu}_3)_2$ in toluene (170 μM , 2 mm path). The inset shows the absorption changes in the Soret region for $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{EtOH})$ in ethanol observed 1 μs after excitation with a 10-ns, 532-nm flash (3 μM , 1 cm path); the ordinate and abscissa for the inset are ΔA and wavelength (nm), respectively.

model has been developed that attempts to correlate this behavior with equatorial π -back-bonding between metal and ring as well as axial π -back-bonding between metal and axial ligands.^{1,2} This model has been tested by extensive picosecond transient absorption studies on a series of Os^{II} porphyrins.^{3,4} Here, we report the results of similar time-resolved measurements on five Ru^{II} porphyrins and one Ru^{III} porphyrin. Our results complement slower time scale studies on Ru^{II} porphyrins^{5,6} and recent picosecond measurements on Ru^{II} porphyrin π -cation radicals.⁷

Experimental Section

The syntheses and purification of the ruthenium porphyrins have been described elsewhere.^{1,8,9} Purity of each sample, prior to use, was checked with thin-layer chromatography, and if necessary, the complexes were chromatographed on a silica gel column to remove any impurities. Samples dissolved in spectral grade solvents were deoxygenated by either bubbling with high purity Ar for >30 min or by repeated freeze-pump-thaw cycles. Concentrations of 50–200 μM were used for the picosecond studies in a 2 mm path length cell through which the sample was flowed. Samples of 1–10 μM in 1-cm cells were employed on the nanosecond apparatus and were changed after several laser shots due to the formation of a photolysis product observed with several of the complexes (see text).

Picosecond transient absorption and kinetic measurements were carried out as described elsewhere.¹⁰ Excitation flashes of 35-ps duration at 532 nm (500 μJ) or 355 nm (300 μJ) were employed. The broad-band (480–900 nm) probe pulses were also of ~ 35 -ps duration. The apparatus was operated at 10 Hz. Each of the reported spectra was acquired from data obtained with 500–1000 laser flashes.

Measurements on the 15 ns to seconds time scale employed a conventional flash photolysis arrangement with 90° pump/probe geometry. A Quantel Datachrom-5000 Q-switched Nd:YAG pumped dye laser system provided excitation pulses of 10-ns duration at the 532-nm or

355-nm Nd:YAG harmonics. Excitation pulse energies were reduced to ≤ 50 mJ. The system was typically operated at 2 Hz for the measurements reported here. Monitoring light was provided by a 300 W Xenon lamp with pre- and post-monochromators having a band-pass of ~ 3 nm. The amplified output of a Hamamatsu R928 PMT was fed into either a Tektronix 468 digital oscilloscope or a 7912AD transient digitizer, both interfaced to a Tektronix 4052A computer. The same setup was used for phosphorescence lifetime measurements.

Absorption spectra were measured on a Cary 14 spectrometer and static emission spectra on a home-built apparatus.

Results

$\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{L})$. We have investigated three carbonyl complexes in which the axial ligand (L) is EtOH, pyridine (py), or 1-methylimidazole (1-Melm). Previous studies on the synthesis, characterization, and equilibrium constants for the formation of these and similar^{1,2,6,8,11–13} complexes show that the L = py or 1-Melm complexes remain hexacoordinate in noncoordinating solvents such as CH_2Cl_2 or toluene. This view is supported by the correspondence of ground-state absorption spectra in toluene and those observed in the presence of excess ligand. For example, the ground-state spectrum of $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{py})$ in toluene or pyridine is essentially the same, having Q(0,0) and Q(1,0) bands at 548 and 518 nm with a peak intensity ratio of ~ 1.5 , as found previously in CH_2Cl_2 .^{1,8} The 1-Melm complex exhibits a similar ground-state spectrum. The (CO)(EtOH), (CO)(py), and (CO)(1-Melm) complexes all exhibit a single Soret band in the range 393–396 nm, also in agreement with previous reports.^{1,8}

Titration experiments⁸ give an equilibrium constant for the association of EtOH to $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})$ in CH_2Cl_2 of $550 \pm 70 \text{ M}^{-1}$. Therefore, in neat CH_2Cl_2 or toluene at the concentrations used, only a few percent of $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{EtOH})$ will be present. In neat EtOH, all the ruthenium will be in the form of the carbonyl(ethanol) complex. The latter species has Q(0,0) and Q(1,0) bands at 548 and 517 nm with an intensity ratio of ~ 2 , in agreement with the literature spectrum.⁸ (The carbonyl complex in the absence of the second axial ligand has similar peak wavelengths but a ratio of ~ 2.7 .) Here, we report studies on the $\text{Ru}(\text{OEP})(\text{CO})(\text{EtOH})$ complex only in neat EtOH.

Figure 1 (solid spectrum) shows an absorption difference spectrum observed 215 ps after excitation of $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{EtOH})$ in ethanol with a 35-ps, 355-nm flash. The spectrum was acquired in four 150-nm slices, which agreed within experimental error in the regions of overlap. Similar absorption changes were observed by using 35-ps, 532-nm flashes in regions where comparisons could be made (560–900 nm). The inset shows the difference spectrum in the Soret-band region observed 1 μs after excitation with a 10-ns flash at 532 nm.

Absorption changes for $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{EtOH})$ in the 460–900 nm region appeared during the 35-ps flash and showed no appreciable decay to 6 ns but did relax, along with the features in the 330–500 nm region on the μs time scale, as discussed below. These absorption changes include bleaching of the Soret band and a broad new absorption decreasing in strength to longer wavelengths (inset). The 215-ps spectrum (solid) shows that this absorption increase tails through bleaching in the ground-state Q bands near 520 and 550 nm and develops into two weak absorption peaks near 720 and 815 nm. Comparison of the magnitude of these features with the absorption changes in the Q-band region, along with the reported extinction coefficients,⁸ indicates that these near-IR transient absorptions have $\log \epsilon \sim 3.7$. The spectral features shown in Figure 1 (solid spectrum) are consistent with those expected for the formation of a metalloporphyrin (π, π^*) excited state,¹⁴ in particular the lowest ring triplet $^3\text{T}(\pi, \pi^*)$.

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Recovery of the Soret-band bleaching at room temperature in deoxygenated ethanol measured on the nanosecond apparatus occurs mainly via a first-order process with a time constant of $\sim 70 \mu\text{s}$. However, the kinetics are complex because there is evidence for a second-order component, possibly due to triplet-triplet annihilation, as well as the formation of a photochemical product that exhibits a shorter lifetime, on the order of $10 \mu\text{s}$.

We also examined the room-temperature emission of $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{EtOH})$ in ethanol and observed phosphorescence at 657 nm and a lifetime of $\sim 80 \mu\text{s}$, in good agreement with decay of the absorption changes. The time-resolved phosphorescence spectrum matched the static emission spectrum.

Spectral and kinetic observations similar to those just described for $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{EtOH})$ in ethanol were found for the $(\text{CO})(\text{py})$ and $(\text{CO})(1\text{-MeIm})$ complexes in toluene and for the $(\text{CO})(\text{py})$ complex in pyridine. The absorption changes and phosphorescence relaxed mainly with a 40–80 μs time constant. Again the decay kinetics were complicated by photochemical products having shorter lifetimes.

The spectral and kinetic results for all three $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{L})$ complexes studied support the assignment of the ${}^3\text{T}(\pi, \pi^*)$ as the lowest excited state. This view has been expressed previously for similar Ru^{II} porphyrins. Hopf et al.^{13b} and Antipas et al.¹ assigned phosphorescence of $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{py})$ at 658 nm (653 nm at 77 K) to the ${}^3\text{T}(\pi, \pi^*)$. Rillema et al.⁶ ascribed phosphorescence at ~ 730 nm and transient absorption changes observed for $\text{Ru}^{\text{II}}(\text{X-TPP})(\text{CO})(\text{Me}_2\text{SO})$ complexes to the ${}^3\text{T}(\pi, \pi^*)$ (X-TPP = para-substituted tetraphenylporphyrin). In the latter study, the triplet decayed with a lifetime of approximately 35 μs at room temperature, and a photochemical product having a shorter lifetime ($\sim 1 \mu\text{s}$) was also observed. On the basis of earlier work on photosubstitution reactions of carbonyl–ruthenium(II) porphyrins,^{13b,15} they assigned the photochemical product as the bis- Me_2SO product, formed upon release of CO followed by binding of a solvent molecule.⁶

$\text{Ru}^{\text{II}}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$. Previous work on this compound in CH_2Cl_2 indicates that the two *P-n-Bu*₃ ligands remain strongly bound in the ground state;⁸ the ground-state absorption spectrum of $\text{Ru}^{\text{II}}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$ in toluene is essentially the same as that reported previously in CH_2Cl_2 .⁸ The spectrum is much different from that of the $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{L})$ compounds discussed above. The bis-*P-n-Bu*₃ complex exhibits visible bands at 512 and 538 nm having a peak ratio of 1.4, while the Soret band is red shifted to 428 nm, and a weaker band of one-quarter the peak intensity is observed at 363 nm.

Figure 1 (dashed spectrum) shows the absorption difference spectrum observed 215 ps after excitation of $\text{Ru}^{\text{II}}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$ in toluene with a 35-ps, 355-nm flash. The spectrum shows bleaching in the visible bands, imbedded on a relatively strong broad absorption between 460 and 650 nm that increases in strength to shorter wavelengths. The dominant spectral feature is the distinct new absorption band near 710 nm. This band and the transient absorption to shorter wavelengths also was observed following excitation with 532-nm flashes. The absorption changes in the 460–650 nm region as well as the absorption peak near 710 nm grew with the instrument response of ~ 35 ps and decayed

with a time constant of 12 ± 3 ns.¹⁶

We assign the transient spectrum observed for $\text{Ru}^{\text{II}}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$ (dashed spectrum in Figure 1) to a $(d, \pi, e_g(\pi^*))$ metal-to-ring CT excited state. Most of the oscillator strength for absorption by this state is expected to come from the porphyrin ring. Since an electron from the metal has been put into one of the ring lowest energy $e_g(\pi^*)$ orbitals, we expect the absorption changes observed upon formation of a (d, π^*) CT to be similar to those found upon formation of a metalloporphyrin π -anion radical. The absorption spectrum for the π -anion radical of $\text{Zn}^{\text{II}}(\text{OEP})$ shows a distinct peak near 710 nm ($\log \epsilon \sim 4$) and broad absorption to shorter wavelengths, extending through the normal Q-band region.¹⁷ These features are in excellent agreement with those just assigned to the (d, π^*) CT for $\text{Ru}^{\text{II}}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$ in Figure 1.¹⁸ The dashed spectrum of Figure 1 is also very similar to that observed previously for $\text{Os}^{\text{II}}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ and assigned to a (d, π^*) CT.^{3,4} The absorption changes for the osmium complex decayed with a time constant of ~ 6 ns,^{3,4} similar to the 12-ns lifetime assigned to the (d, π^*) CT for $\text{Ru}^{\text{II}}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$ in the present study.

$\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$. The ground-state absorption spectrum of this compound in toluene is similar to that reported previously in 3-methylpentane.¹ The Q(1,0) and Q(0,0) bands are at 539 and 572 nm, and the Soret-band maximum is at 392 nm; there is also a weaker absorption peak at 345 nm and a strong shoulder near 420 nm on the long-wavelength side of the Soret band, extending to approximately 480 nm. Absorption difference spectra at several time delays with respect to excitation with a 35-ps, 355-nm flash are shown in Figure 2A. The spectra show broad absorption extending to 650 nm and bleachings in the ground-state visible bands. Measurements on this sample at longer wavelengths using either 355- or 532-nm excitation pulses did not reveal any distinct new peaks between 650 and 780 nm. The absorption changes decayed by about half the maximum amplitude observed during the excitation flash with a lifetime of ≤ 35 ps, while the slower component requires > 5 ns to relax. The small amplitude of the second component prevented a more accurate determination of the lifetime.

Assignment of the transient state(s) responsible for the spectra observed for $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ in Figure 2A is less clear than that for the other complexes discussed above. The absorption changes between 550 and 650 nm are very similar to those reported previously for $\text{Os}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ and $\text{Os}^{\text{II}}(\text{OEP})(\text{NO})_2$, in studies employing 6-ps flashes at 532 nm.^{3,4} The evolution of the absorption changes also is similar. Both osmium complexes exhibited fast decays of 36 and ≤ 9 ps, respectively, and slower decays of 6 and 9 ns. The fast components were ascribed to intersystem crossing ${}^1\text{Q}(\pi, \pi^*) \rightarrow {}^3\text{T}(\pi, \pi^*)$. The nitrosonium methoxide also showed an initial 15-ps step, believed to be due to relaxation in the singlet manifold.^{3,4} On the basis of the spectral and kinetic resemblances with these two osmium porphyrins, we tentatively assign the ≤ 50 ps and > 5 ns components observed in the present study for $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ to the ${}^1\text{Q}(\pi, \pi^*)$ and ${}^3\text{T}(\pi, \pi^*)$ states. However, these assignments must be discussed within the context of previous absorption and emission studies.^{1,2}

It has been reported that the ${}^3\text{T}(\pi, \pi^*)$ for $\text{Os}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ emits at 77 K (lifetime $\sim 125 \mu\text{s}$), while $\text{Os}^{\text{II}}(\text{OEP})(\text{NO})_2$

(14) (a) On the basis of work on other metalloporphyrins in which the lowest excited states are (π, π^*) in origin (see ref 3, 6, 14b–i and references therein for examples), we expect the (π, π^*) excited states to exhibit the following features in the 450–650 nm region: OEP complexes should show broad featureless absorption broken by bleachings in the ground-state Q-bands, while TPP complexes should show a strong new absorption between 450 and 500 nm, tailing through the Q-band bleachings to near 650 nm. The (π, π^*) states of both macrocycles may show one or two weak new absorption peaks between 700 and 900 nm. (b) Magde, D.; Windsor, M. W.; Holten, D.; Gouterman, M. *Chem. Phys. Lett.* **1974**, *29*, 183–188. (c) Pekkarinen, L.; Linschitz, H. *J. Am. Chem. Soc.* **1960**, *82*, 2407–2411. (d) Cornelius, P. A.; Steele, A. W.; Chernoff, D. A.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1981**, *82*, 9–14. (e) Fujita, I.; Netzel, T.; Chang, C. K.; Wang, C.-B. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 413–417. (f) Reynolds, A. H.; Straub, K. D.; Rentzepis, P. M. *Biophys. J.* **1982**, *40*, 27–31. (g) Kim, D.-H.; Holten, D.; Gouterman, M. *J. Am. Chem. Soc.* **1984**, *106*, 2793–2798. (h) Kim, D.-H.; Holten, D.; Gouterman, M.; Buchler, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 4015–4017. (i) Kalyanasundaram, K. *Chem. Phys. Lett.* **1984**, *104*, 357–362.

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(16) Since we could monitor to only ~ 12 ns on the picosecond apparatus, this lifetime was obtained from fits to the data using a single exponential decay assuming the absorption changes go to zero at the asymptote. The same lifetime to within the reported error was obtained when the asymptote was fit along with the rest of the decay curve, in which case $\Delta A \approx 0$ at long times was found.

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(18) In addition to the 710-nm peak, the π -anion radical of $\text{Zn}^{\text{II}}(\text{TPP})$ shows a second new peak near 910 nm, not found for $\text{Zn}^{\text{II}}(\text{OEP})$. As expected, we did not find this additional peak for $\text{Ru}^{\text{II}}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$ when the spectrum of Figure 1 was extended to 930 nm. Therefore, an additional peak near 910 nm is expected in the absorption difference spectrum for $\text{Ru}^{\text{II}}(\text{TPP})(\text{P-}n\text{-Bu}_3)_2$.

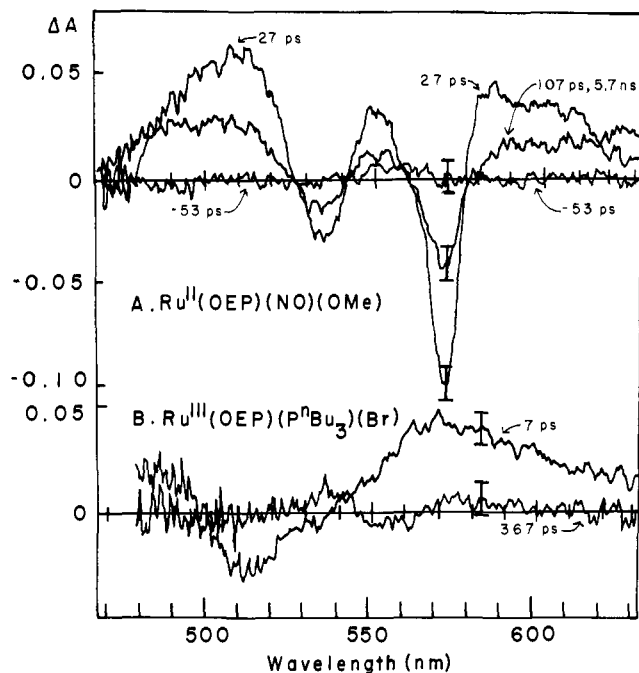


Figure 2. (A) Absorption changes observed for $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ in toluene at several time delays with respect to the peak of the 35-ps, 355-nm flash. Spectra at 107 ps and 5.7 ns are the same within experimental error. The -53-ps spectrum gives a measure of the base line and shows that no unrelaxed transients remain in the excited volume between laser shots. (B) Absorption changes observed for $\text{Ru}^{\text{III}}(\text{OEP})(\text{P}-n\text{-Bu}_3)(\text{Br})$ in CH_2Cl_2 at two time delays with respect to the 35-ps, 355-nm flash. The absorption changes decay in ≤ 35 ps.

and $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ are dark.^{1,2} The lack of 77 K emission in the last two compounds was rationalized on the basis of IEH calculations that predicted CT transitions $\text{ring}(\pi) \rightarrow [\text{metal } d_\pi + \text{NO}(\pi^*)]$ at lower energy than for $\text{Os}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$. As discussed above and previously,¹ the UV-vis ground-state absorption spectrum of $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ shows extra bands not of (π, π^*) origin. It was argued¹ that the presence of these $[\pi, d_\pi + \text{NO}(\pi^*)]$ states, nearby in energy to the lowest (π, π^*) states, might act to quench emission. From the picosecond measurements,⁴ it was suggested that the short (6–9 ns) lifetimes attributed to the $^3\text{T}(\pi, \pi^*)$ in $\text{Os}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ and $\text{Os}^{\text{II}}(\text{OEP})(\text{NO})_2$ might be due to thermal population of such CT states. Therefore, it is possible that the >5 ns decay we observed for $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ also involves relaxation of the $^3\text{T}(\pi, \pi^*)$ via similar CT states. In fact, mixing of the $^3\text{T}(\pi, \pi^*)$ with nearby CT states could be the reason why the spectra of Figure 2A are somewhat different from those of Figure 1 assigned above to $^3\text{T}(\pi, \pi^*)$ and (d, π^*) states of $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{L})$ and $\text{Ru}^{\text{II}}(\text{OEP})(\text{P}-n\text{-Bu}_3)_2$, respectively.

An additional possibility is that the >5 ns absorption changes could contain a component from a deligated species. There is evidence that $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ also may be photochemically active. A very weak transient decaying in the millisecond range is observed after excitation on the nanosecond apparatus. However, the small amplitude of these absorption changes and those due to the >5 -ns component observed on the picosecond apparatus (Figure 2A) make it difficult to assign these transients to the same species. Possibly, population of a $[\pi, d_\pi + \text{NO}(\pi^*)]$ state from the $^3\text{T}(\pi, \pi^*)$ in $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ causes release of the NO ligand in low yield.

$\text{Ru}^{\text{III}}(\text{OEP})(\text{P}-n\text{-Bu}_3)(\text{Br})$. A previous study⁸ on this compound in CH_2Cl_2 has shown that the bromide ion is coordinated to the central metal. It was also shown that the metal contained one unpaired electron, consistent with a half-filled d_π orbital expected for the d^5 Ru^{III} ion. The ground-state absorption spectrum, observed here and previously,⁸ exhibits near-UV peaks at 410 and 363 nm (peak ratio ~ 1.6), a broad $^1\text{Q}(\pi, \pi^*)$ band centered at 512 nm, and a near-IR peak ($\log \epsilon \sim 3$) at 710 nm.

Excitation of this complex in CH_2Cl_2 with a 35-ps, 355-nm flash

gave the weak absorption changes shown in Figure 2B. The transient decayed during the excitation flash, putting an upper limit of <35 ps on the lifetime. Deconvolution procedures indicate that the lifetime is probably <20 ps.

The state responsible for the 710-nm absorption band in the ground-state spectrum is probably also responsible for the rapid excited-state quenching. A similar near-IR absorption band has been assigned in a number of Co^{II} porphyrins to an allowed ring-to-metal ($a_{2u}(\pi), d_{z^2}$) CT. Quenching by this low-lying state is thought to be responsible for the lack of emission from these complexes and is predicted to be in the right energy range on the basis of IEH calculations.¹⁹ Picosecond studies on several Co^{II} porphyrins in noncoordinating solvents^{20,21} have shown that the excited-state deactivation occurs in <35 ps and involves a transient which shows new absorption resembling that observed here for the Ru^{III} complex (Figure 2B). This transient in the Co^{II} complexes was assigned as the (π, d_π) CT.²¹ Picosecond studies have shown that the same type of CT state lies along the excited-state relaxation pathway in $\text{Co}^{\text{III}}(\text{OEP})(\text{CN})$,²¹ as predicted.¹⁹ Low-lying metal \leftrightarrow ring CT states are thought to be responsible for the rapid (<35 ps) relaxations observed following excitation of $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{L})$ π -cation radicals.⁷

Our results on $\text{Ru}^{\text{III}}(\text{OEP})(\text{P}-n\text{-Bu}_3)(\text{Br})$ indicate that a similar deactivation pathway may exist in this complex. The most probable state responsible for the 710-nm ground-state band, the <35 -ps kinetics, and the transient spectrum of Figure 2B is a $(a_{2u}(\pi), d_\pi)$ ring-to-metal CT. The absorption difference spectra for such CT states are expected to be similar to those for the formation of the metalloporphyrin π -cation radical. The spectrum of Figure 2B is consistent with the assignment, based on π -cation radical spectra for ruthenium porphyrins.^{8,22} However, the small amplitude of the absorption changes makes a firm spectral characterization difficult in this case.

Therefore, on analogy to the behavior found for other porphyrins just mentioned, it is reasonable to assign the quenching state in $\text{Ru}^{\text{III}}(\text{OEP})(\text{P}-n\text{-Bu}_3)(\text{Br})$ to a (π, d_π) CT. It should be noted that such a state would not be expected to provide quenching in Ru^{II} porphyrins, because the d_π orbitals are filled.

Discussion

Assignment of the transient states responsible for the photochemical behavior of the ruthenium porphyrins we have investigated has been discussed along with the presentation of the results. Here we wish to consider how these observations and interpretations fit the π -back-bonding model developed for the d^6 metalloporphyrins.^{1,2} This model has been applied to recent picosecond results on osmium porphyrins.^{3,4}

In the d^6 metalloporphyrins, the filled metal d_{xy} and $d_\pi(d_{xz}, d_{yz})$ orbitals have energy comparable to the highest filled porphyrin ring orbitals $a_{1u}(\pi)$ and $a_{2u}(\pi)$.^{1,2} Thus, the Ru^{II} porphyrins are expected to have a $(d_\pi, e_g(\pi^*))$ metal-to-ring CT state in the same energy range as the lowest ring triplet, $^3\text{T}(\pi, \pi^*)$.^{1,2} It has been argued that the relative energies of these states should be influenced strongly by equatorial π -back-bonding between metal d_π and empty ring $e_g(\pi^*)$ orbitals as well as by axial π -back-bonding between the metal d_π and the π^* orbitals on the axial ligands.^{1,2} The result of the equatorial interaction is a lowering of the energy of the d_π orbitals and an increase in the energy of the ring $e_g(\pi^*)$ orbitals; this raises the energy of both the ring (π, π^*) and metal-to-ring $(d_\pi, e_g(\pi^*))$ states. A hypsochromic (blue) shift in the ground-state visible (π, π^*) absorption bands compared to complexes d^n ($n < 6$) is a manifestation of the effect on the $e_g(\pi)$ orbitals.^{1,2}

Addition of an axial ligand capable of accepting electron density

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from the d_{π} orbitals will decrease the amount of equatorial π -back-bonding to the porphyrin ring and, thus, diminish the increase in energy of the (π, π^*) states due to equatorial π -back-bonding. However, the axial π -back-bonding will result in increased stabilization of the d_{π} , maintaining the increased energy of the $(d_{\pi}, e_g(\pi^*))$ CT state over its position with no π -back-bonding interaction. A change from equatorial-to-axial π -back-bonding, then, should decrease the energy of the ${}^3T(\pi, \pi^*)$ state while leaving the energy of the $(d_{\pi}, e_g(\pi^*))$ CT state relatively unchanged.

Therefore, the model suggests that whether the lowest excited electronic state in the Ru^{II} porphyrins is the ${}^3T(\pi, \pi^*)$ or the $(d_{\pi}, e_g(\pi^*))$ can be modulated by the use of different axial ligands.^{1,2} Absorption and emission measurements and IEH calculations on a series of Ru^{II} porphyrins support this view,^{1,2} as do similar studies^{1,2} and picosecond experiments^{3,4} on Os^{II} porphyrins. The results of the picosecond investigations reported here for several Ru^{II} complexes also are in agreement with the predictions of the π -back-bonding model.

The effects of π -back-bonding on the photophysical behavior are most readily illustrated by comparing the assignment of the lowest excited states for the $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{L})$ complexes vs. $\text{Ru}^{\text{II}}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$. The π -back-bonding between Ru and the axially bound CO will have two effects: (1) It will reduce equatorial π -back-bonding between the metal and the porphyrin ring. This should lower the energy of the $e_g(\pi^*)$ orbitals and hence the ${}^3T(\pi, \pi^*)$ excited state. (2) Good Ru-CO axial π -back-bonding will push down the d_{π} orbitals in energy, thus maintaining or raising the energy of the $(d_{\pi}, e_g(\pi^*))$ CT state. The net effect of the Ru-CO back-bonding is a lowering of the ${}^3T(\pi, \pi^*)$ relative to the metal-to-ring (d, π^*) CT. We have assigned absorption difference spectra of Figure 1 (solid and inset) to the ${}^3T(\pi, \pi^*)$ in the three $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{L})$ complexes, L = EtOH, py, or 1-MeIm. The $\sim 75 \mu\text{s}$ relaxation kinetics measured by decay of room temperature absorption changes and emission are consistent with the ${}^3T(\pi, \pi^*)$ as the lowest excited state. The same conclusion has been drawn previously from photophysical studies on these or similar Ru^{II} porphyrins, as mentioned above.^{2,6,13,15}

Compared to CO, P-*n*-Bu₃ is a weaker π -acceptor and much stronger σ -donor.²³ Thus removal of CO as an axial ligand and

the concomitant change in importance from axial-to-equatorial π -back-bonding at the metal has the effect of raising the energy of the ${}^3T(\pi, \pi^*)$ relative to the (d, π^*) CT. The absorption difference spectrum observed upon excitation of this complex has the characteristics of a porphyrin metal-to-ring CT, as discussed above. The 12-ns lifetime also is consistent with the assignment of the (d, π^*) CT as the lowest excited state of this molecule.

Considering now $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$, the nitrosonium ion, NO^+ , is an even stronger axial π -back-bonding ligand than is CO. The additional effect from the σ -donating OMe ligand establishes a push-pull bonding stabilization for the complex,² and a red shift of the ${}^1Q(\pi, \pi^*)$ ground-state absorption band (compared to the CO complexes) results from this bonding scheme. The Q bands for the $(\text{NO})(\text{OMe})$ complex are at 532 and 572 nm, while they are at 517 and 548 nm for the $(\text{CO})(\text{L})$ complexes studied here, as discussed in the Results section. Therefore, we expect that that for $\text{Ru}^{\text{II}}(\text{OEP})(\text{NO})(\text{OMe})$ the ${}^3T(\pi, \pi^*)$ will be lower in energy relative to the (d, π^*) as compared to $\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})(\text{L})$. We assign the $<50 \text{ ps}$ and $\geq 5 \text{ ns}$ decays in the absorption changes (Figure 2A) to ${}^1Q(\pi, \pi^*) \rightarrow {}^3T(\pi, \pi^*)$ and ${}^3T(\pi, \pi^*)$ relaxation, respectively. This interpretation is similar to that given for the analogous Os^{II} complex.^{3,4} However, as pointed out above, the previous absorption measurements and the lack of 77 K emission provide evidence that predicted¹ $[(\pi, d_{\pi} + \text{NO}(\pi^*))]$ CT states may be involved in the triplet decay.¹

Finally, the $\text{Ru}^{\text{III}}(\text{OEP})(\text{P-}n\text{-Bu}_3)(\text{Br})$ complex has a half-filled d_{π} orbital, giving the possibility of a low-energy ring \rightarrow metal (π, d_{π}) CT excited state. This state may be responsible for the weak 710-nm band observed in the ground-state absorption spectrum. The presence of this low-energy quenching state appears to dominate the photophysical behavior, and it results in rapid relaxation in $\leq 35 \text{ ps}$.

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Product Branching in Infrared Multiple Photon Decomposition of Gas-Phase Ions. Mechanistic Implications for Proton-Transfer Reactions

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Abstract: Negative ions that lie on potential surfaces for proton-transfer reactions have been photolyzed in the gas phase with an infrared laser. The relative photodissociation yields of reactants and products of the proton-transfer reactions as well as the kinetics of the reactions themselves have been measured. The results provide details about the potential surfaces, mechanisms, and thermochemistry of these reactions.

Reactive intermediates are highly elusive,¹ but a complete understanding of a reaction mechanism necessitates knowledge of the structure and energetics of such species. Chemically activated intermediates such as those which occur in low-pressure,

gas-phase, ion-molecule reactions are especially interesting, because very little is known about them. The purpose of this work has been to probe potential surfaces of ion-molecule reactions (in particular, proton-transfer reactions) by means of infrared pho-

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