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)(L1)(L2)). The ruthenium(II) porphyrins are of three types. First are the carbonyl complexes in which L1 = CO and L2 = EtOH, pyridine (py), or 1-methylimidazole (1-Melim), which all exhibit similar spectral and kinetic behavior. The lowest excited states of these molecules are assigned as the ring \(3^T(\pi,\pi^*)\) in agreement with previous work on similar complexes. The \(3^T(\pi,\pi^*)\) 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 \(\epsilon\) ~ 3.7) near 720 and 815 nm; these features are consistent with the assignment of the transient as a metalloporphyrin \((\pi,\pi^*)\) triplet. The \(1^Q(\pi,\pi^*)\) lifetimes in these carbonyl complexes appear to be <35 ps. Different photophysical behavior is observed for RuII(OEP)(P-n-Bu3). 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 \((d,\pi^*)\) CT excited state on the basis of resemblances with ground-state spectra of metalloporphyrin \(\pi\)-anion radicals. The absorption changes observed upon excitation of RuII(OEP)(NO)(OMe) in toluene with a 35-ps flash decay in two steps, with lifetimes of \(\leq 50\) ps and >5 ns. These components are tentatively assigned to relaxation of the ring \(1^Q(\pi,\pi^*)\) and \(3^T(\pi,\pi^*)\) excited states. The triplet decay may proceed via ring \((\pi) \rightarrow [\text{metal } d_\pi + \text{NO}(\pi^*)]\) CT states predicted to be in the proper energy range from previous theoretical work. Finally, excited RuII(OEP)(P-n-Bu3)(Br) decays completely in \(\leq 35\) ps, possibly via a \((\pi,d_\alpha)\) ring-to-metal CT excited state. Our results are discussed in terms of recent absorption and emission measurements and calculations on d6 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 FeII, RuII, and OsII porphyrins. These investigations have shown that the electronic properties of these complexes are strongly affected by the \(\sigma\)-donating and \(\pi\)-accepting nature of axial ligands. The relative energies of the lowest ring \((\pi,\pi^*)\) 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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Results

Ru(II)(OEP)(CO)(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 complexes show that the L = py or 1-Melm complexes remain hexacoordinate in noncoordinating solvents such as CH2Cl2 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 Ru(II)(OEP)(CO)(py) in toluene or pyridine is essentially the same, having Q(0,0) and Q(1,0) bands at 548 and 516 nm with a peak intensity ratio of ~1.5, as found previously in CH2Cl2.1,8 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 experiments give an equilibrium constant for the association of EtOH to Ru(II)(OEP)(CO) in CH2Cl2 of ~50 ± 30 M−1. Therefore, in neat CH2Cl2 or toluene at the concentrations used, only a few percent of Ru(II)(OEP)(CO)(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 516 nm with an intensity ratio of ~1.5, in agreement with the literature.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 Ru(OEP)(CO)(EtOH) complex only in neat EtOH.

Figure 1 (solid spectrum) shows an absorption difference spectrum observed 215 ps after excitation of Ru(II)(OEP)(CO)(EtOH) in ethanol with a 35-ps, 355-nm flash. The spectrum was acquired in four 150-ns 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 Ru(II)(OEP)(CO)(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 indicate 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, indicates that these near-IR transient absorptions have log ε ~ 3.7. The spectral features shown in Figure 1 (solid spectrum) are consistent with those expected for the formation of a metallacorphyrin (x,π+) excited state, in particular the lowest ring triplet (3π(x,π+)).
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 ~70 μs. However, the kinetics are complex because there is evidence for a second-order component, possibly due to triplet-triplet annihilation as well as the photophysical product that exhibits a shorter lifetime, on the order of 10 μs.

We also examined the room-temperature emission of RuII-(OEP)(CO)(EtOH) in ethanol and observed phosphorescence at 657 nm and a lifetime of ~80 μs, 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 RuII-(OEP)(CO)(EtOH) in ethanol were found for the (CO)(py) and (CO)(1-MeIm) complexes in toluene and for the (CO)(py) complex in pyridine. The absorption changes and phosphorescence relaxed mainly with a 40-μs μs time constant. Again the decay kinetics were complicated by photochemical products having shorter lifetimes.

The spectral and kinetic results for all three RuII(OEP)(CO)(L) complexes studied support the assignment of the T(π,π*) state as the lowest excited state. This view has been expressed previously for similar RuII porphyrins. Hopf et al.13 and Antipas et al.14 assigned phosphorescence of RuII(OEP)(CO)(py) at 658 nm (653 nm at 77 K) to the T(π,π*). Rillema et al.15 assigned phosphorescence at ~730 nm and transient absorption changes observed for RuII(X-TPP)(CO)(Me2S0) complexes to the T(π,π*) (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 (~1 μs) was also observed. On the basis of earlier work on photosubstitution reactions of carboxyl–ruthenium(II) porphyrins,13,15 they assigned the photochemical product as the bis-μ2-S0 product, formed upon release of CO followed by binding of a solvent molecule.6

RuII(OEP)(P-n-Bu)3. Previous work on this compound in CH3Cl2 indicates that the two P-n-Bu ligands remain strongly bound in the ground state,6 the ground-state absorption spectrum of RuII(OEP)(P-n-Bu)3 in toluene is essentially the same as that reported previously in CH3Cl2.6 The spectrum is much different from that of the RuII(OEP)(CO)(L) compounds discussed above. The bis-P-n-Bu complex exhibits visible bands at 512 and 538 nm, having a ratio of 1:4, while the Soret band is broad 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 RuII(OEP)(P-n-Bu)3 in toluene with a 35-ps, 355-nm flash. The spectrum shows bleaching in the visible bands, imbedded on a relatively strong broad featureless absorption broken by bleachings in the ground-state Q-bands, 650 nm. The spectrum matched the static emission spectrum. CH2Cl2 indicates that the two n-Bu complexes studied support the assignment of the lowest excited state. This view has been expressed previously for phyrins,13b·15 complexes to the CT for RuII(OEP)(P-n-Bu)3 in the present study.

RuII(OEP)(NO)(MeO). The ground-state absorption spectrum of this compound in toluene is similar to that reported previously in 3-methylpentane.7 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 RuII(OEP)(NO)(MeO) 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 OsII(OEP)(NO)(OMe) and OsII(OEP)(N02), in studies employing 6-ps flashes at 532 nm.14 The evolution of the absorption changes also is similar. Both osmium complexes exhibited fast decays of 36 and 59 ps, respectively, and slower decays of 6 and 9 ns. The fast components were assigned to intersystem crossing Q(π, π*) → T(π, π*). The nitrosonium methoxide also showed an initial 15-ns step, believed to be due to relaxation in the singlet manifold.14 On the basis of the spectral and kinetic similarities with these two osmium porphyrins, we tentatively assign the ~50 ps and >5 ns components observed in the present study for RuII(OEP)(NO)(OMe) to the Q(π, π*) and T(π, π*) states. However, these assignments must be discussed within the context of previous absorption and emission studies.12

It has been reported that the T(π, π*) for OsII(OEP)(NO)-(OMe) emits at 77 K (lifetime ~125 μs), while OsII(OEP)(NO)
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Figure 2. (A) Absorption changes observed for RuII(OEP)(NO)(OMe) in toluene at several time delays with respect to the peak of the 35-ns, 355-nm flash. Spectra at 107 ps and 5.7 ns are the same within experimental error. The -33-ns 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 RuII(OEP)(P-n-Bu3)(Br) in CH2Cl2 at two time delays with respect to the 35-ns, 355-nm flash. The absorption changes decay in ≤35 ps and RuII(OEP)(NO)(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 rising (π → [metal d0 + NO(π*)]) at lower energy than for OsIII(OEP)-(NO)(OMe). As discussed above and previously,1,2 the UV-vis ground-state absorption spectrum of RuII(OEP)(NO)(OMe) shows extra bands not of (π,π*) origin. It was argued1 that the presence of these π, dπ + NO(π*) 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 (5-9 ns) lifetimes attributed to the T(π,π*) in OsIII(OEP)(NO)(OMe) and OsIII(OEP)(NO)2 might be due to thermal population of such CT states. Therefore, it is possible that the >5-ns decay we observed for RuII(OEP)(NO)(OMe) also involves relaxation of the T(π,π*) via similar CT states. In fact, mixing of the T(π,π*) 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 T(π,π*) and (dπ,π*) states of RuII(OEP)(CO)(L) and RuII(OEP)(P-n-Bu3)Br, respectively.

An additional possibility is that the >5-ns absorption changes could contain a component from a deligated species. There is evidence that RuII(OEP)(NO)(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 π, dπ + NO(π*)] state from the T(π,π*) in RuII(OEP)(NO)(OMe) causes release of the NO ligand in low yield.

RuIII(OEP)(P-n-Bu3)(Br). A previous study9 on this compound in CH2Cl2 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 dπ orbital expected for the d5 RuIII ion. The ground-state absorption spectrum, observed here and previously,5 exhibits near-UV peaks at 410 and 363 nm (peak ratio ~1.6), a broad Q(π,π*) band centered at 512 nm, and a near-IR peak (log ε ~ 3) at 710 nm.

Excitation of this complex in CH2Cl2 with a 35-ns, 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 CoII porphyrins to an allowed ring-to-metal (αα,αd,αd) 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 CoII porphyrins in noncoordinating solvents20,21 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 RuII complex (Figure 2B). This transient in the CoII complexes was assigned as the (π,π*) CT.21 Picosecond studies have shown that the same type of CT state lies along the excited-state relaxation pathway in CoIII(OEP)(CN)2 as predicted.19 Low-lying metal ↔ ring CT states are thought to be responsible for the rapid (<35 ps) relaxations observed following excitation of RuII(OEP)(CO)(L) π-cation radicals.7

Our results on RuII(OEP)(P-n-Bu3)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 (αα,αd,αd) 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.12,12 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 RuII(OEP)(P-n-Bu3)Br to a (π,π*) CT. It should be noted that such a state would not be expected to provide quenching in RuIII porphyrins, because the dπ orbitals are filled.

Discussion

Assignment of the transient states responsible for the photophysical 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 d6 metalloporphyrins.1,2 This model has been applied to recent picosecond results on osmium porphyrins.1,4

In the d6 metalloporphyrins, the filled metal dπ and dπ(eπ→eg(π*)) orbitals have energy comparable to the highest filled porphyrin orbitals and empty ring eg(π*) orbitals as well as by axial π-back-bonding between the metal dπ and the π* orbitals on the axial ligands.1,2 The result of the equatorial interaction is a lowering of the energy of the dπ orbitals and an increase in the energy of the ring eg(π*) orbitals; this raises the energy of both the ring (π,π*) and metal-to-ring (dπ,eg(π*)) states. A hypochromic (blue) shift in the ground-state visible (π,π*) absorption bands compared to complexes dπ (n < 6) is a manifestation of the effect on the eg(π*) orbitals.1,2

Addition of an axial ligand capable of accepting electron density

from the dπ 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 dπ, maintaining the increased energy of the (dπ,eπ(π*)) 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(π,π*) state while leaving the energy of the (dπ,eπ(π*)) CT state relatively unchanged.

Therefore, the model suggests that whether the lowest excited electronic state in the RuII porphyrins is the 3T(π,π*) or the (dπ,eπ(π*)) can be modulated by the use of different axial ligands. Absorption and emission measurements and IEH calculations on a series of RuII porphyrins support this view, as do similar studies and picosecond experiments on OsII porphyrins. The results of the picosecond investigations reported here for several RuII 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 RuII(OEP)(CO)(L) complexes vs. RuII(OEP)(P-n-Bu3)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 eπ(π*) orbitals and hence the 1T(π,π*) excited state. (2) Good Ru-CO axial π-back-bonding will push down the dπ orbitals in energy, thus maintaining or raising the energy of the (dπ,eπ(π*)) CT state. The net effect of the Ru-CO back-bonding is a lowering of the 3T(π,π*) relative to the metal-to-ring (π,π*) CT. We have assigned absorption difference spectra of Figure 1 (solid and inset) to the 3T(π,π*) excited state of the RuII(OEP)(CO)(L) complexes, L = EtOH, py, or 1-Melm. The ~75 µs relaxation kinetics measured by decay of room temperature absorption changes and emission are consistent with the 3T(π,π*) as the lowest excited state. The same conclusion has been drawn previously from photophysical studies on these or similar RuII porphyrins, as mentioned above.

Compared to CO, P-n-Bu3 is a weaker π-acceptor and much stronger σ-donor. 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(π,π*) relative to the (dπ,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 (dπ,π*) CT as the lowest excited state of this molecule.

Considering now RuII(OEP)(NO)(OME), the nitrosionium 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, and a red shift of the 1Q(π,π*) ground-state absorption band (compared to the CO complexes) results from this bonding scheme. The Q bands for the (NO)(OME) complex are at 532 and 572 nm, while they are at 517 and 548 nm for the (CO)(L) complexes studied here, as discussed in the Results section. Therefore, we expect that that for RuII(OEP)(NO)(OME) the 3T(π,π*) will be lower in energy relative to the (dπ,π*) as compared to RuII(OEP)(CO)(L). We assign the <50 ps and ≥5 ns decays in the absorption changes (Figure 2A) to 1Q(π,π*) → 3T(π,π*) and 3T(π,π*) relaxation, respectively. This interpretation is similar to that given for the analogous OsII complex. However, as pointed out above, the previous absorption measurements and the lack of 77 K emission provide evidence that predicted [(π, dπ + NO(π*))] CT states may be involved in the triplet decay.

Finally, the RuIII(OEP)(P-n-Bu3)(Br) complex has a half-filled dπ orbital, giving the possibility of a low-energy ring → metal (π, dπ) 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 ≤35 ps.

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