J. Phys. Chem. 1988, 92, 714–720

Axial-Ligand Control of the Photophysical Behavior of Ruthenium(II) Tetraphenyl- and Octaethylporphyrin. Contrasting Properties of Metalloporphyrin (π,π^*) and (d,π^*) Excited States

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(Received: June 15, 1987; In Final Form: September 9, 1987)

The photophysical behavior of the ruthenium(II) porphyrins depends dramatically on the axial ligands coordinated to the central metal ion. We have measured the picosecond and slower time scale transient absorption spectra and kinetics, emission data, and ground-state absorption spectra for two classes of complexes: RuP(CO)(L) and RuP(L)$_2$. Results are compared for complexes in which the porphyrin macrocycle (P) is tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP) and the axial ligand L is piperidine (pip), pyridine (py), dimethyl sulfoxide (Me$_2$SO), or ethanol (EtOH). We assign the lowest excited state of all the RuP(CO)(L) complexes, including those with L absent, as the lowest excited triplet state, $^3(\pi,\pi^*)$, of the porphyrin ring. $^3(\pi,\pi^*)$ appears to form in high yield from the ring excited singlet, $^1(\pi,\pi^*)$, in $\leq$30 ps. On the other hand, we assign the lowest excited state of the RuP(L)$_2$ complexes, except for RuTPP(Me$_2$SO)$_2$, as a metal-to-ring (d,π^*) charge-transfer (CT) state. We attribute this general switch of the lowest excited state from $^3(\pi,\pi^*)$ in RuP(CO)(L) to (d,π^*) in RuP(L)$_2$ to the loss of π-backbonding between the filled Ru(dπ) orbitals and the empty CO(π^*) orbitals. The loss of axial π-backbonding is expected to destabilize the dπ orbitals, making them closer in energy to the empty e$_g$(π^*) orbitals of the porphyrin ring. This lowers the energy of (d,π^*) relative to $^3(\pi,\pi^*)$ in RuP(L)$_2$ compared to RuP(CO)(L). Although $^3(\pi,\pi^*)$ appears to be the lowest excited state in all the RuP(CO)(L) complexes investigated, we propose that the deactivation of this state nonetheless proceeds, in part, via a shorter lived (d,π^*) state at higher energy. We speculate that the faster decay of (d,π^*) compared to $^3(\pi,\pi^*)$ may be due to a better Franck–Condon factor for radiationless decay to the ground state. The decay route of $^3(\pi,\pi^*)$ via a thermally accessible (d,π^*) in the RuP(CO)(L) complexes also may be the pathway for photodissociation of CO from these molecules, which in the presence of L results in the formation of RuP(L)$_2$. The photodissociation quantum yield is measured to be $\sim 10^{-4}$ for two of the complexes.

Introduction

In recent years ruthenium and osmium porphyrins have been investigated as models for the biologically important iron porphyrin complexes.[1-10] These second- and third-row homologues have also received special attention because of the marked effects of the two axial ligands on the electronic properties and reactions of the complexes. Of central importance in Ru(II) porphyrin chemistry is the π-accepting carbon monoxide (CO) ligand. This ligand has a dramatic influence on synthetic procedures and substitutional lability of the sixth (trans) ligand,[1-6] site of electrochemical oxidation,[2,3,6,7] photodissociation behavior,[3c,5,8] porphyrin ring vibrational frequencies,[9] and electronic absorption[3,5] and emission behavior,[5,10] and apparently on the nature of the lowest excited state.[5,10]

Most of these observations have been rationalized in terms of the ability of the CO ligand to accept π-electron density from the metal dπ orbitals, thus lowering the energy of the dπ orbitals relative to the π-HOMO's of the porphyrin ring. This π-backbonding model has been put on a more firm footing by recent molecular orbital calculations on a series of d^6 metalloporphyrins.[5] This model has been used to explain the results of recent transient absorption and kinetic studies from our laboratory on several Ru(II) porphyrins.[10] For three CO-containing complexes, RuOEP(CO)(L) [OEP = octaethylporphyrin and L = ethanol (EtOH), pyridine (py), or 1-methylimidazole], the lowest excited state was assigned as the lowest triplet state, $^3(\pi,\pi^*)$, of the porphyrin ring. On the other hand, the lowest excited state of RuOEP(PBu$_3$)$_2$ was assigned as a metal-to-ring (d,π^*) charge-transfer (CT) state. Effective d$\pi \rightarrow$ CO(π^*) backbonding apparently lowers the energy of the dπ orbitals in these RuOEP(CO)(L) complexes to the extent that (d,π^*) is raised above $^3(\pi,\pi^*)$.

We felt that it would be useful to expand these studies to include RuP(CO)(L) and RuP(L)$_2$ complexes that contain the same L, so that direct comparisons could be made. In addition, we wished to examine the effects of both the porphyrin macrocycle and the σ-donating and π-accepting abilities of the axial ligands on the photophysical behavior of the Ru(II) porphyrins. Here we report the results of such investigations using time-resolved and steady-state optical techniques. We have studied two series of Ru(II) porphyrins: RuP(CO)(L) and RuP(L)$_2$, with P = OEP or TPP (tetraphenylporphyrin) and L = piperidine (pip), py, dimethyl sulfoxide (Me$_2$SO), or EtOH. We have paid particular attention to the spectral and kinetic characterization of the lowest excited state of each complex. We assign the lowest excited state as $^3(\pi,\pi^*)$ for all the RuP(CO)(L) complexes and (d,π^*) CT for all but one of the RuP(L)$_2$ complexes. However, we propose that even in the RuP(CO)(L) complexes a (d,π^*) CT state, thermally accessible from $^3(\pi,\pi^*)$, may have significant effect on the photophysical behavior.

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Experimental Section

Complexes. The (CO)(EtOH) and (CO)(py) complexes of RuOEP and RuTPP were purchased from Porphyrin Products. Solutions of RuOEP(CO) and RuTPP(CO) were prepared by dissolving the corresponding RuP(CO)(EtOH) complexes in CH_2Cl_2. RuOEP(CO)(EtOH) and RuTPP(CO)(EtOH), which would otherwise dissociate[2a] to give RuOEP(CO) and RuTPP(CO), were investigated in neat EtOH. RuOEP(CO)(L) and RuTPP(CO)(L) [L = Me_2SO, pip, and py] were prepared by dissolving the RuP(CO)(EtOH) complexes in the appropriate neat ligating solvent. These complexes could be isolated and redissolved, intact, in noncoordinating solvents.[1-6] The electronic absorption spectra of the complexes RuOEP(CO)(L) [L = absent,[2a] EtOH,[2a] Me_2SO,[3c] py[2a,3c,5]] and RuTPP(CO)(L) [L = absent,[4b,c,6a] py[3a]] were found to agree with literature spectra. The NMR spectrum of RuOEP(CO)(py) in $CDCl_3$ or benzene-d_6 was found to agree with the literature spectrum.[5]

The RuOEP$(L)_2$ and RuTPP$(L)_2$ complexes were prepared by photolyzing the corresponding RuP(CO)(L) compounds in either a sealed degassed solution or an Ar-bubbled solution of neat ligand L until the absorption spectrum of the precursor RuP(CO)(L) complex was replaced by that of the RuP$(L)_2$ complex. This procedure is quantitative for strongly binding ligands such as py, pip, and Me_2SO, and the RuP$(L)_2$ complexes can be readily isolated and purified.[1c,2,3c,5] The NMR spectrum of RuOEP$(py)_2$ in pyridine-d_6 or $CDCl_3$ was found to agree with the literature spectrum.[1b] The electronic absorption spectra of the complexes RuOEP$(L)_2$ [L = Me_2SO,[3c] py[3c,5]] and RuTPP$(py)_2$[3a] were found to agree with the literature spectra. Time-resolved studies were generally carried out in the neat ligating solvent (L) or in CH_2Cl_2.

We present preliminary measurements of the RuP$(EtOH)_2$ complexes, which we did not attempt to isolate and characterize other than by the UV/vis spectra in neat EtOH, which were in accord with the expectations based on the other RuP$(L)_2$ complexes. We plan more extensive studies of RuP$(L)_2$ complexes containing such weakly binding ligands, for which the preferred preparative route is via the metal-metal-bonded dimers.[1]

Dichloromethane was distilled from CaH_2; pyridine was dried over KOH and distilled from CaH_2 under Ar. Piperidine was distilled under Ar immediately before use. Spectral grade Me_2SO and absolute EtOH were used without further purification.

Measurements. Picosecond transient absorption spectra and kinetics were carried out as described elsewhere,[11] and employed 30-ps, 532-nm, 750 μJ–2 mJ excitation flashes at 5 Hz. Samples (~150 μM) were either flowed through a 2 mm path length cell or sealed in 2 mm path length cells following repeated freeze–pump–thaw cycles on a high-vacuum line. Nanosecond–millisecond measurements were performed on an apparatus described elsewhere,[10] and employed 10-ns excitation flashes at either 532 or 355 nm at 2 Hz. For these measurements, ~1 μM samples were degassed and sealed in 1-cm cells.

Ground-state absorption spectra were recorded on a Cary 14 or a Perkin-Elmer Model 330 spectrophotometer. Low-temperature (77 K) phosphorescence spectra of samples in EPA (diethyl ether:isopentane:EtOH = 5:5:2) in 1-cm cells were recorded on a home-built apparatus employing a 90° geometry and a Hamamatsu R928 photomultiplier tube. Actinometric measurements were preformed using the ferrioxalate technique basically as described elsewhere.[8,12] The output of a 100-W xenon lamp was passed through infrared-absorbing and interference (400, 410, or 550 nm) filters and illuminated samples in CH_2Cl_2 in a thermostated (23 °C) cell. NMR spectra were acquired on a Varian 300-MHz FT spectrometer.

Results

Ground Electronic State Absorption Spectra. Electronic absorption spectra of most of the Ru(II) porphyrins that we investigated have been reported previously (see Experimental Section). For a given macrocycle (P), relatively small changes in the spectra occur in the RuP(CO)(L) complexes as the sixth ligand L is varied; i.e., the changes are small compared to those induced by replacement of the CO ligand or by a change in macrocycle. For the RuOEP(CO)(L) series, L = absent < EtOH < Me_2SO < py < pip, the Soret band shifts from 393 to 397 nm, the Q(1,0) band from 512 to 519 nm, and the Q(0,0) band from 547 to 550 nm. Similar shifts in peak positions are observed in the RuTPP(CO)(L) series; the Soret band shifts from 410 to 412 nm, the Q(1,0) band from 529 to 531 nm, and the Q(0,0) band from 561 to 565 nm. The sixth ligand L also affects the peak intensity ratio of the Q bands.[2a,6b] A more detailed analysis of the ground-state absorption spectra of the RuP(CO)(L) complexes can be found elsewhere.[13]

The ground electronic state absorption spectrum, as well as the photophysical behavior in general, is strongly perturbed upon replacement of the π-backbonding CO ligand by a relatively strong σ-donor ligand such as py or pip. For example, compared to RuOEP(CO)(py) the intensity of the Soret band of RuOEP$(py)_2$ is reduced and the Soret, Q(1,0), and Q(0,0) bands are blue-shifted to 393, 492, and 520 nm respectively.[3c,5] Similar spectral changes are seen for the corresponding TPP complexes,[3a] and for both macrocycles the $(py)_2$ and $(pip)_2$ complexes have essentially the same spectra. On the other hand, both RuP$(Me_2SO)_2$ complexes exhibit differences in their absorption spectra compared to the other RuP$(L)_2$ complexes. For example, as reported previously,[3c] the Soret band of RuOEP$(Me_2SO)_2$ is slightly red-shifted and has comparable intensity to that of RuOEP(CO)(Me_2SO). The Q bands of RuOEP$(Me_2SO)_2$ are broad and intermediate in position between those of the RuOEP(CO)(L) complexes and RuOEP$(py)_2$ or RuOEP$(pip)_2$. As discussed below, we believe that the Me_2SO ligands may display some π-accepting character, thus giving the ground-state absorption spectrum (and other photophysical behavior) of RuOEP$(Me_2SO)_2$ and RuTPP$(Me_2SO)_2$ some of the character of the Ru(CO)(L) complexes.

Photochemistry of the Carbonyl Complexes. The conversion RuP(CO)(L) → RuP$(L)_2$ can be achieved by irradiation in the appropriate coordinating solvent, L.[1-3,5,8] Previous room temperature measurements of the conversion of RuTPP(CO)(pip) to RuTPP$(pip)_2$ in piperidine gave a quantum yield of 2.5×10^{-6} for irradiation at 530 nm and 5.9×10^{-5} for irradiation at 410 nm.[8] The quantum yield was found to be somewhat higher (1.5×10^{-4}) for excitation at either wavelength at 80 °C. The quantum yield for formation of RuOEP$(py)_2$ from RuOEP(CO)(py) has been estimated to be $\sim 1 \times 10^{-4}$ for Soret-band excitation.[3c] We obtained the same quantum yield ($(1.0 \pm 0.2) \times 10^{-4}$) for the latter process at 23 °C using Soret-band (400 nm) excitation and the ferrioxalate actinometric technique.[12] We also examined the conversion of RuTPP(CO)(py) to RuTPP$(py)_2$ in pyridine. The quantum yield was found to be $(1.9 \pm 0.3) \times 10^{-4}$ with irradiation in the Q bands (550 nm) and $(1.8 \pm 0.3) \times 10^{-4}$ for irradiation in the Soret band (410 nm). Thus, we did not observe an excitation wavelength dependence of the quantum yield for photolysis of RuTPP(CO)(py).

Emission Results. Phosphorescence spectra at 77 K in EPA were measured for the RuP(CO)(py) and RuP(CO)(pip) complexes. The emission spectrum for RuOEP(CO)(pip) is essentially the same as that for RuOEP(CO)(py) observed in this study and reported previously.[3c,5,10] The spectrum exhibits a maximum at 653 nm with weaker, overlapping bands having maxima near 715 and 725 nm. The phosphorescence spectra for the corresponding TPP complexes are also virtually identical with one another, exhibiting a maximum at 721 nm and a weaker band centered near 810 nm. Phosphorescence near 730 nm has been reported previously for Ru(X-TPP)(CO)(Me_2SO), where X-TPP is para-substituted TPP.[7]

Room temperature phosphorescence was also measured for RuOEP(CO)(py) and RuTPP(CO)(py) in degassed pyridine at 1 μs following excitation with a 10-ns flash at 532 nm. The

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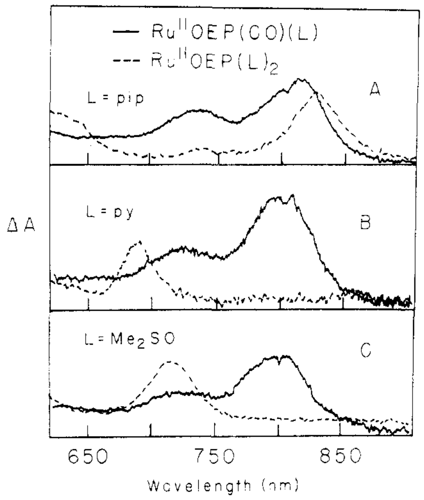

Figure 1. Transient difference spectra for the RuOEP complexes measured 50 ps after a 30-ps 532-nm flash. The abscissa in each panel represents $\Delta A = 0$. Samples generally did not have the same concentration, so the absolute magnitudes of the absorption changes for the various complexes should not be compared. (The maximum ΔA for each spectrum is between 0.08 and 0.3.) The dashed spectra in panels A, B, and C were measured in CH$_2$Cl$_2$, CH$_2$Cl$_2$, and Me$_2$SO, respectively. The spectrum for RuOEP(CO)(pip) in panel A was found to be the same in pip and CH$_2$Cl$_2$. The spectrum for RuOEP(CO)(py) in panel B was found to be the same in py, 10% py in CH$_2$Cl$_2$, and CH$_2$Cl$_2$. The solid spectra in panels A, B, and C were measured in pip, py, and Me$_2$SO, respectively. The spectrum for RuOEP(py)$_2$ was found to be the same in py and CH$_2$Cl$_2$. Each spectrum represents the average of data acquired with ~300 excitation flashes and has an error in ΔA of approximately ±0.005.

time-resolved emission spectra in the major bands (near 655 and 720 nm for the two complexes, respectively) agree well with the 77 K steady-state spectra. The emission decay times for both molecules were found to be ~35 μs at room temperature. This lifetime agrees with the kinetics measured via transient absorption, which are discussed below.

Excited-State Absorption Spectra. Figure 1 shows transient-state difference spectra in the 600- to 900-nm region for six of the RuOEP complexes, measured 50 ps after excitation with a 30-ps, 532-nm flash. Each panel compares spectra for the RuOEP(CO)(L) complex (solid) and RuOEP(L)$_2$ complex (dashed): panel A for L = pip, panel B for L = py, and panel C for L = Me$_2$SO. Spectra for the corresponding RuTPP complexes are shown in Figure 2. Since the ground states of the molecules do not absorb beyond 600 nm, the difference spectrum for each complex corresponds to the absorption spectrum of the excited state present at 50 ps. On the basis of the magnitude of the transient absorption compared to the Q-band bleachings (not shown), we estimate that the main excited-state absorption band in the near-infrared has an extinction coefficient in the range 10^3–10^4 M^{-1} cm^{-1} for all the complexes.

The excited-state spectra for all the RuOEP(CO)(L) complexes develop with the 30-ps excitation flash and remain unchanged in shape and amplitude between 50 ps and 12 ns, the longest time delay on our picosecond spectrometer. The transient absorptions decay on the microsecond time scale, as discussed below. The transient absorption spectrum we measured for RuOEP(CO)(EtOH) (not shown) is the same as that reported previously from our laboratory[10] and is very similar to that of RuOEP(CO)(py) complex in (Figure 1B, solid). The excited-state spectra are not particularly solvent dependent. For example, the spectrum for RuOEP(CO)(py) is essentially the same in CH$_2$Cl$_2$, in 10% pyridine in CH$_2$Cl$_2$, and in neat pyridine. It is seen in Figure 1 that all of the RuOEP(CO)(L) complexes have similar excited-state spectra, with a relatively strong band near 800 nm and a smaller absorption maximum near 720 nm. This data suggests that the same, or a similar, excited state (most likely $^3(\pi,\pi^*)$; see below) is responsible for the transient absorption spectrum in each of these CO-containing complexes.

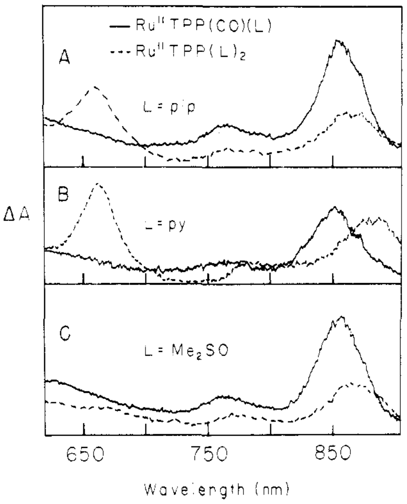

Figure 2. Transient difference spectra for the RuTPP complexes. The conditions are the same as in Figure 1. The spectra for selected compounds were found to be essentially independent of solvent (see Figure 1 legend).

The 50-ps spectra in the same spectral region for the RuOEP(L)$_2$ complexes (Figure 1, dashed) also grow with the 30-ps 532-nm excitation flash, but decay on the 10–100-ns time scale, as discussed below. The spectrum for the RuOEP(py)$_2$ complex exhibits a prominent absorption band near 690 nm (Figure 1B, dashed). This band is red-shifted to 715 nm for RuOEP(Me$_2$SO)$_2$ (Figure 2C, dashed). These spectra are similar to that reported previously for RuOEP(PBu$_3$)$_2$, which exhibited a transient absorption maximum near 710 nm.[10] The spectrum for RuOEP(pip)$_2$ (Figure 1A, dashed), acquired on a more concentrated sample, shows more well-resolved features beyond 700 nm. Unlike the other RuOEP(L)$_2$ complexes, the transient spectrum for RuOEP(pip)$_2$ does not contain a strong absorption maximum near 700 nm in either pip or CH$_2$Cl$_2$, but rather exhibits absorption increasing in strength toward shorter wavelengths. Spectra between 500 and 600 nm, acquired with 355-nm excitation flashes (not shown), did not reveal any clear absorption maxima in this region either.

The general characteristics of the spectra for the TPP complexes are similar to those just described for the OEP complexes. The 50-ps spectra for all the RuTPP(CO)(L) complexes are similar, as indicated by the spectra for L = pip, py, and Me$_2$SO in Figure 2 (solid), and for L = EtOH (not shown). The strong band near 800 nm and the weaker one near 760 nm are both red-shifted by about 50 nm as compared to positions in the spectra of the RuOEP(CO)(L) complexes. Again the absorption changes for the RuTPP(CO)(L) compounds grow with the 30-ps flash and decay on the microsecond time scale (see below).

The excited-state spectra for RuTPP(pip)$_2$ and RuTPP(py)$_2$ are also different from the spectra for the RuTPP(CO)(L) complexes (see Figure 2, A and B). Spectra for the former two molecules exhibit a well-resolved absorption band near 650 nm, and weaker absorptions near 770 and 870 nm.

Finally, the excited-state spectrum for RuTPP(Me$_2$SO)$_2$ in Figure 2C is similar to that for RuTPP(CO)(Me$_2$SO), rather than being similar to those of the other RuTPP(L)$_2$ complexes (Figure 2A, B, dashed). This spectral difference for RuTPP(Me$_2$SO)$_2$, in fact, correlates with the kinetic data. The decay time of photoexcited RuTPP(Me$_2$SO)$_2$ is 1.6 μs, whereas the other RuTPP(L)$_2$ complexes decay with lifetimes of ≤100 ns, as we now discuss.

Excited-State Decay Kinetics. Typical kinetic profiles for the decay of photoexcited RuP(CO)(L) complexes are shown in Figure 3A–D. First-order lifetimes for the RuTPP(CO)(L) complexes (including L = absent) are in a rather narrow range of 24–47 μs (Table I). The value of 40 μs for RuTPP(CO)(Me$_2$SO) (Figure 3D) is in good agreement with that of 36 μs reported previously from emission and transient absorption studies.[7] The lifetimes for the five RuOEP(CO)(L) complexes were found to be in the

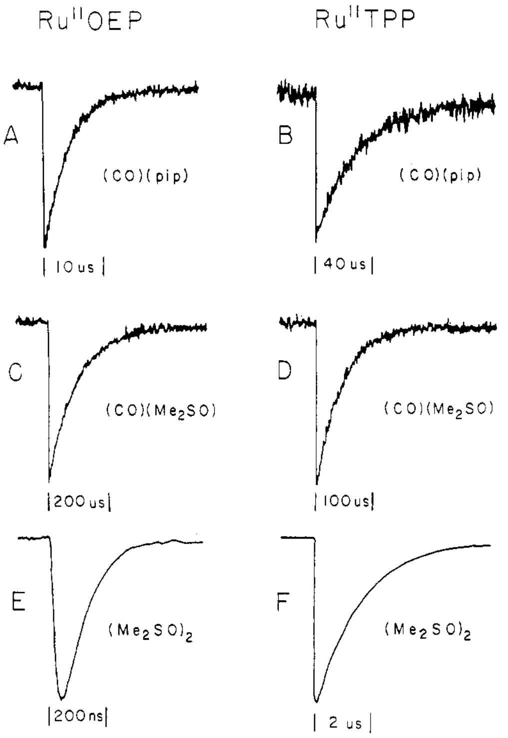

Figure 3. Decay of bleaching ($\Delta A \sim 0.1$) at the Soret band maximum (390–415 nm). Degassed samples having concentrations of ~1 µM in the neat solvent (either pip or Me$_2$SO) were excited with a 10-ns flash at 532 nm. Traces A–D were acquired by using 1–10 flashes, traces E and F with 32 flashes.

TABLE I: Excited-State Lifetimes for Ruthenium(II) Porphyrins[a]

complex	solvent	lifetime
RuOEP(CO)	CH$_2$Cl$_2$	55 ± 2 µs
RuOEP(CO)(EtOH)	EtOH	~50 µs
RuOEP(CO)(Me$_2$SO)	Me$_2$SO	93 ± 3 µs
RuEP(CO)(py)	py	34 ± 5 µs
	3-MP[b]	26 ± 2 µs
RuOEP(CO)(pip)	pip	4 ± 1 µs
	3-MP[b]	6 ± 1 µs
RuOEP(Me$_2$SO)$_2$	Me$_2$SO	93 ± 6 ns
RuOEP(py)$_2$	py	15 ± 3 ns
RuOEP(pip)$_2$	pip	1.7 ± 0.2 ns
RuTPP(CO)	CH$_2$Cl$_2$	47 ± 4 µs
RuTPP(CO)(EtOH)	EtOH	37 ± 1 µs
RuTPP(CO)(Me$_2$SO)	Me$_2$SO	40 ± 1 µs
RuTPP(CO)(py)	py	35 ± 5 µs
RuTPP(CO)(pip)	pip	24 ± 4 µs
RuTPP(Me$_2$SO)$_2$	Me$_2$SO	1.6 ± 0.5 µs
RuTPP(py)$_2$	py	15 ± 2 ns
RuTPP(pip)$_2$	pip	2.0 ± 0.2 ns

[a] Measured in degassed solution at room temperature. [b] 3-Methylpentane.

range 4–93 µs. The values for RuOEP(CO)(EtOH) and RuOEP(CO)(py) are in agreement with those reported previously.[10]

Substantially shorter decay times were generally found for the RuP(L)$_2$ complexes. Figure 4 (circles) shows a log plot for decay of the strong transient absorption band near 660 nm for RuTPP(py)$_2$ (see Figure 2B, dashed), observed using 30-ps 532-nm excitation flashes. At the longest time delay on our picosecond apparatus (12 ns), the absorption increase has decayed to about 50% of its initial value. The plot shown in Figure 4, which yields a lifetime of 15 ± 2 ns, assumes that the asymptote of the decay is zero (i.e., $\Delta A_\infty = 0$). That this is the case was confirmed by measurements which showed that no absorption changes remain in the visible or near-infrared regions of the spectrum at 50 ns after a 10-ns flash. Similarly, decay of the absorption increase observed near 680 nm for RuOEP(py)$_2$ (see Figure 1B, dashed) is first order with a time constant of 15 ± 3 ns (decay plot not shown).

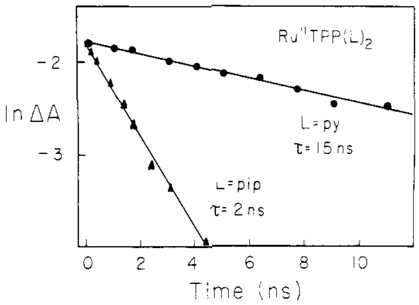

Figure 4. Log plot showing decay of the absorbance increase near 650 nm (see Figure 2) for RuTPP(py)$_2$ in pyridine (●) and RuTPP(pip)$_2$ in piperidine (▲), using 30-ps 532-nm excitation flashes. The ΔA at each delay time had an error of approximately ±0.005. The solid lines are linear least-squares fits to $\ln(\Delta A) = -t/\tau$. Similar time constants were obtained from nonlinear least-squares fits of the raw data to an arbitrary constant (ΔA_∞) plus an exponential, which also gave a fitted $\Delta A_\infty \sim 0$.

The two RuP(pip)$_2$ complexes exhibit even shorter lifetimes than the RuP(py)$_2$ complexes. Time constants of 2.0 ± 0.2 and 1.7 ± 0.2 ns were measured for RuTPP(pip)$_2$ and RuOEP(pip)$_2$, respectively. A log plot for the decay of the 660-nm transient absorption band of RuTPP(pip)$_2$ (see Figure 2A, dashed) is shown in Figure 4 (triangles).

The two RuP(Me$_2$SO)$_2$ complexes have significantly longer excited-state lifetimes than the other RuP(L)$_2$ complexes. There is also a larger difference in lifetime between the two macrocycles. Excited RuOEP(Me$_2$SO)$_2$ decays with a time constant of 93 ns (Figure 3E) and RuTPP(Me$_2$SO)$_2$ with a lifetime of 1.6 µs (Figure 3F). The latter decay time is the same as that observed previously in emission and transient absorption studies of photolyzed RuTPP(CO)(Me$_2$SO) in Me$_2$SO and assigned to decay of the photoexcited RuTPP(Me$_2$SO)$_2$ photoproduct.[7] Preliminary measurements on RuOEP(EtOH)$_2$ and RuTPP(EtOH)$_2$ gave excited-state lifetimes of ~35 and ~50 ns, respectively.

Discussion

Assignment of the Lowest Excited State of RuP(CO)(L) Complexes. The results of this study reinforce the view expressed in the Introduction that the CO ligand plays a dominant role in ruthenium porphyrin chemistry. In particular all ten of the RuP(CO)(L) complexes investigated here exhibit very similar photophysical behavior. The ground-state spectra for a given macrocycle are similar, being only weakly dependent on the sixth ligand (L). The excited-state lifetimes fall in the range 4–93 µs (Table I). The emission spectra we observed for the RuP(CO)(py) and RuP(CO)(pip) complexes can be assigned as phosphorescence from the ring lowest excited triplet state, $^3(\pi,\pi^*)$. This agrees with previous assignments of the emission from RuOEP(CO)(py),[5,10] and RuTPP(CO)(Me$_2$SO).[7]

Transient absorption spectra for the RuOEP(CO)(L) complexes (Figure 1, solid) are only weakly dependent on the nature (or presence) of the sixth ligand L. All these spectra are similar to the spectrum of RuOEP(CO)(EtOH) obtained earlier in our laboratory and assigned to $^3(\pi,\pi^*)$.[10] The transient absorption spectra for the RuTPP(CO)(L) complexes (Figure 2, solid) also are only weakly dependent on the sixth ligand and are very similar to the spectrum reported some time ago for $^3(\pi,\pi^*)$ of ZnTPP.[14] In fact, the present study provides further evidence, in agreement with an increasing body of data, that such double-banded near-infrared transient absorption spectra, red-shifted by ~50 nm for TPP compared to OEP, are characteristic of $^3(\pi,\pi^*)$ spectra.[15,16] Thus on the basis of all the available spectral and kinetic data, we assign $^3(\pi,\pi^*)$ as the lowest excited state of all the RuP-

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(CO)(L) complexes that we have investigated.

The lifetime of the lowest excited singlet state, $^1(\pi,\pi^*)$, of the RuP(CO)(L) complexes appears to be <30 ps. The observed absorption changes (Figures 1 and 2), just assigned to $^3(\pi,\pi^*)$, appear coincident with the 30-ps flash. Within our temporal resolution there is no indication of an earlier state, such as $^1(\pi,\pi^*)$. (In this regard we paid special attention to the growth of near-infrared absorption changes; in the $^1(\pi,\pi^*)$ spectra of a number of metalloporphyrins the relatively strong band near 800 nm for OEP and near 850 nm for TPP is reduced in amplitude.[15,16]) The lack of fluorescence, together with the fast rise time and magnitude of the near-infrared absorptions, is consistent with rapid and efficient $^1(\pi,\pi^*) \rightarrow {}^3(\pi,\pi^*)$ intersystem crossing for all of the RuP(CO)(L) complexes. Undoubtedly, effective spin–orbit coupling involving the central Ru(II) ion plays a role here.

A spin–orbit effect may also be responsible, at least in part, for the short (microsecond time scale) $^3(\pi,\pi^*)$ lifetimes of the RuP(CO)(L) complexes compared to the millisecond time scale lifetimes of other metalloporphyrin complexes, such as those of Zn(II) and Mg(II).[17] Although the phosphorescence yield for RuOEP(CO)(py) has been estimated to be relatively high (6×10^{-2}),[5] nonradiative pathways dominate the deactivation of $^3(\pi,\pi^*)$. One nonradiative route is direct intersystem crossing from $^3(\pi,\pi^*)$ to the ground state. Another possible nonradiative decay route of $^3(\pi,\pi^*)$ is thermal population of a state at higher energy which itself deactivates rapidly to the ground state. We give arguments below that a (d,π^*) CT state, thermally accessible from $^3(\pi,\pi^*)$, probably contributes substantially to the excited-state dynamics of the RuP(CO)(L) complexes.

Assignment of the Lowest Excited State of RuP(L)$_2$ Complexes. The excited-state lifetimes of the RuP(L)$_2$ complexes are strongly dependent on the nature of the axial ligand (Table I). Except for the two RuP(Me$_2$SO)$_2$ complexes, the lifetimes for a given ligand are similar for the OEP and TPP macrocycles. The lifetime of 1.6 μs for excited RuTPP(Me$_2$SO)$_2$ is significantly longer than that of 93 ns for RuOEP(Me$_2$SO)$_2$ and approaches the range observed for the RuP(CO)(L) complexes (Table I). Thus, except for RuTPP(Me$_2$SO)$_2$, the excited-state decay rates of the RuP(L)$_2$ complexes are substantially higher than for the RuP(CO)(L) complexes, for L = py or pip, by a factor of 10^3–10^4!

This dramatic reduction in lifetime upon removal of the CO ligand is most easily explained if, in the RuP(L)$_2$ complexes, the lowest excited state is not the ring $^3(\pi,\pi^*)$, but rather is a metal-to-ring (d,π^*) CT excited state. We suggest that this is the case in all the RuP(L)$_2$ complexes except RuTPP(Me$_2$SO)$_2$. The transient absorption spectra are consistent with this view. Consider RuTPP(py)$_2$ and RuTPP(pip)$_2$. The 50-ps transient absorption spectra (Figure 2A, B, dashed) are in excellent agreement with the spectrum of the π-anion radical of ZnTPP, which exhibits a relatively strong band ($\epsilon \sim 1.3 \times 10^4$ M^{-1} cm^{-1}) near 700 nm, a weaker band ($\epsilon \sim 4 \times 10^3$ M^{-1} cm^{-1}) near 800 nm, and a third band ($\epsilon \sim 1 \times 10^4$ M^{-1} cm^{-1}) near 900 nm.[18,19] We expect similarities in spectra of π-anion radicals and (d,π^*) CT states due to similarities in their electronic configurations: In the π-anion radical an electron is added to one of the ring e$_g$(π^*) LUMO's; the ring HOMO's, a$_{1u}$(π) and a$_{2u}$(π), remain filled. The same porphyrin-ring orbital populations are obtained upon the transfer of an electron from a metal orbital to a ring e$_g$(π^*) LUMO, i.e., upon the formation of a metal-to-ring (d,π^*) CT excited state. Therefore, on the basis of the transient absorption spectra, and the short lifetimes, we assign the lowest excited state of RuTPP(py)$_2$ and RuTPP(pip)$_2$ [and tentatively of RuTPP(EtOH)$_2$] as a (d,π^*) CT.

We draw a similar conclusion for the RuOEP(L)$_2$ complexes. The π-anion radicals of ZnEtio and MgEtio have pronounced absorptions near 650 and 860 nm, with a weaker band near 770 nm.[18,20,21] (The π-anion radicals of etioporphyrin (Etio) are expected to have spectra similar to the OEP π-anion radicals.) The transient absorption spectra for RuOEP(py)$_2$ (Figure 1B, dashed) shows a distinct peak near 670 nm, with some indication of much weaker bands near 780 and 860 nm. The prominent 670-nm band is red-shifted to 710 nm for RuOEP(EtOH)$_2$ (not shown) and to 715 nm for RuOEP(Me$_2$SO)$_2$ (Figure 2C, dashed). On the basis of this apparent shift in the "anion" band with the σ-donor strength of the ligand, one might expect the band to lie to the blue of 650 nm for RuOEP(pip)$_2$. Therefore, that the band is not observed in this complex can be explained if it is masked by bleaching in the Q-bands or by the broad absorption below 660 nm. The transient absorption spectra for the RuOEP(L)$_2$ complexes do not generally show the pronounced band near 850 nm observed in the spectra of the π-anions of ZnEtio or ZnTPP,[18-21] or in the transient absorption spectra for RuTPP(L)$_2$ complexes. Thus, although the transient absorption spectra for all the RuOEP(L)$_2$ complexes do not agree feature for feature with the literature π-anion radical spectra, they are much different than those of the RuOEP(CO)(L) compounds. (RuOEP(pip)$_2$ is inconsistent with any of the spectral patterns, as noted above.) The excited-state lifetimes of the RuOEP(L)$_2$ complexes are also substantially shorter than those of the RuP(CO)(L) compounds. Therefore, on the basis of the combined spectral and kinetic data, we assign (d,π^*) CT as the lowest excited state of the RuOEP(L)$_2$ complexes, as we have for all but one of the RuTPP(L)$_2$ compounds.

The exception among the RuP(L)$_2$ complexes is RuTPP(Me$_2$SO)$_2$. The transient absorption spectrum (Figure 2C, dashed) does not contain the "anion" peak near 660 nm. Instead this complex has a double-banded spectrum (Figure 2C) which, except for a 10-nm red shift, resembles the spectrum assigned to $^3(\pi,\pi^*)$ in RuTPP(CO)(Me$_2$SO). On the basis of this data, and the microsecond time scale decay time, we assign the lowest excited state of RuTPP(Me$_2$SO)$_2$ as $^3(\pi,\pi^*)$. The shorter 1.6 μs lifetime of $^3(\pi,\pi^*)$ in this complex compared to lifetimes of 24–47 μs for the RuTPP(CO)(L) complexes can be understood in terms of a thermally activated decay route. If (d,π^*) in RuTPP(Me$_2$SO)$_2$ is closer in energy above $^3(\pi,\pi^*)$ than in the RuTPP(CO)(L) complexes (see below), then it would provide a more effective pathway for deactivation. The different ground-state and transient-state spectra and kinetics for RuTPP(Me$_2$SO)$_2$ compared to the other RuTPP(L)$_2$ complexes can be rationalized if the Me$_2$SO ligands are π-backbonded to by the metal, i.e., have some π-accepting ability. This would give the axial ligands in RuTPP(Me$_2$SO)$_2$ some of the character of the CO in the RuTPP(CO)(L) complexes. Similarly, some π-accepting behavior of the Me$_2$SO ligands could account for the fact that RuOEP(Me$_2$SO)$_2$ has a somewhat different ground-state absorption spectrum and longer (93 ns) lifetime than observed for RuOEP(py)$_2$ and RuOEP(pip)$_2$. That the Ru(II) ion in RuOEP(Me$_2$SO)$_2$[3c] and the metal ion in other transition-metal complexes[22] can π-backbond to Me$_2$SO has been suggested previously.

Effects of Axial Ligands on the Orbital Energies of Ru(II) Porphyrins. The difference in the photophysical behavior of the RuP(CO)(L) and RuP(L)$_2$ complexes can be discussed within the context of previous molecular orbital calculations and the associated π-backbonding model.[5] For the Ru(II) porphyrins one must consider *equatorial* π-backbonding involving the filled metal dπ orbitals and the empty ring e$_g$(π^*) orbitals, and *axial* π-backbonding involving the filled metal dπ orbitals and the empty π^* orbitals on the Co axial ligand. The first consequence of axial π-backbonding is that it should diminish the metal → ring

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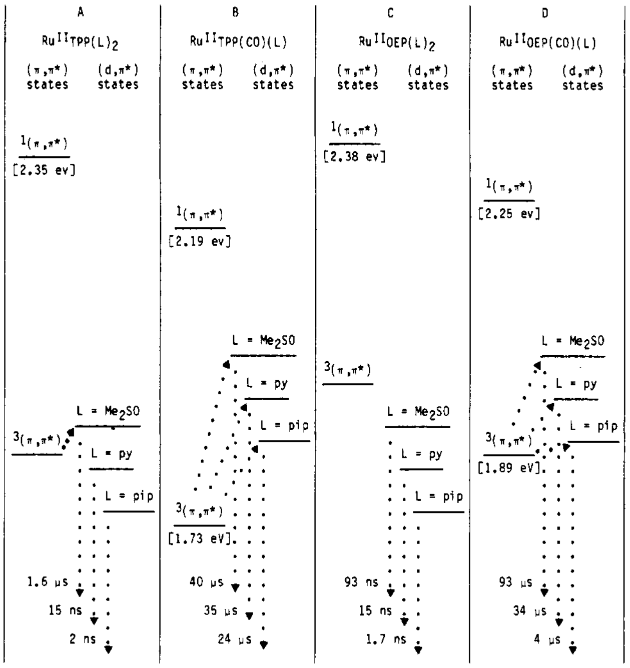

Figure 5. Proposed ordering of the excited states for the Ru(II) porphyrins. The energies of states known from absorption or emission experiments are given in brackets. See text for discussion.

equatorial π-backbonding, resulting in a lowering in the energy of the ring $e_g(\pi^*)$ orbitals in the RuP(CO)(L) complexes. This suggests that the ground-state (π,π^*) absorption bands of the RuP(CO)(L) complexes should be at lower energy than those of the corresponding $RuP(L)_2$ complexes, as is observed (see Results). Second, the axial π-backbonding should further stabilize the metal dπ orbitals. Thus, the energy of the metal-to-ring $(d_\pi, e_g(\pi^*))$ CT is expected to increase relative to the ring $^3(\pi,\pi^*)$ in the RuP(CO)(L) complexes compared to the $RuP(L)_2$ complexes. This shift is in the direction consistent with our assignments of the lowest excited states based on the results of our time-resolved measurements.

Proposed Energy Level Ordering and Deactivation Pathways. Figure 5 shows tentative excited-state energy level diagrams for the four major types of complexes that we investigated. In each complex the $^1(\pi,\pi^*)$ energy is known from the position of the Q(0,0) absorption band. For each RuP(CO)(L) complex the $^3(\pi,\pi^*)$ energy is known from the phosphorescence origin. Since the $RuP(L)_2$ complexes are generally nonluminescent, we have assumed that the $^1(\pi,\pi^*)$–$^3(\pi,\pi^*)$ gap is roughly the same as in the RuP(CO)(L) complexes. We also assume that (d,π^*) for a given L has roughly the same energy whether the macrocycle is TPP or OEP. (The ring is easier to reduce in TPP, but the metal is harder to oxidize.[18]) Based on the results of our time-resolved spectral and kinetic measurements, we place (d,π^*) above $^3(\pi,\pi^*)$ in all the RuP(CO)(L) complexes and (d,π^*) below $^3(\pi,\pi^*)$ in all the $RuP(L)_2$ complexes, except for $RuTPP(Me_2SO)_2$. The energy of (d,π^*) may decrease as the σ-donor strength of the axial ligand L increases along the series Me_2SO, py, pip, since the added electron density at the metal should destabilize the filled metal dπ and d_{xy} orbitals, decreasing the energy gap between these orbitals and the (higher energy) ring empty $e_g(\pi^*)$ orbitals. This trend is consistent with the observed decrease in lifetime (increase in decay rate) along the ligand series for a given type of complex (Table I and Figure 5). Thus, although we do not know the absolute energies of many of the excited states, we believe that the ordering of the levels shown in Figure 5 allows a reasonable interpretation of the results.

The dotted lines in Figure 5 show the decay processes that we believe are largely responsible for the observed excited-state lifetimes. For the $RuP(L)_2$ complexes, except $RuTPP(Me_2SO)_2$, we propose that the lifetime is associated with decay of (d,π^*) directly to the ground state. For the RuP(CO)(L) complexes we propose that the lifetime is the inverse of the sum of three rates. Two deactivation pathways, phosphorescence and intersystem crossing, return $^3(\pi,\pi^*)$ directly to the ground state. The third is a thermally activated pathway via a nearby short-lived (d,π^*) state. The participation of the latter, indirect, decay route is consistent with four observations: (1) We have found a decrease in the lifetime of $^3(\pi,\pi^*)$ in the RuP(CO)(L) complexes as the σ-donor strength of L increases; as discussed above, (d,π^*) may progressively drop closer in energy to $^3(\pi,\pi^*)$, thus increasing the deactivation rate. (2) The 34-μs room temperature excited-state lifetime of RuOEP(CO)(py) (Table I) is substantially shorter than the value of 405 μs measured previously via phosphorescence decay at 77 K.[5] (3) A state thermally accessible from $^3(\pi,\pi^*)$ appears to be responsible for the dissociation of CO in these complexes.[8] (4) It has been observed that the $^3(\pi,\pi^*)$ lifetime varies with the Hammett σ-parameter of the para phenyl substituent in a series of $Ru(tetraarylporphyrin)(CO)(Me_2SO)$ complexes;[7] phenyl substitution should change the energy of the (d,π^*) state. We believe that the thermally activated route for deactivation via (d,π^*) is important in determining the $^3(\pi,\pi^*)$ lifetime in photoexcited RuP(CO)(L) complexes.

Although the trends in the lifetime of the lowest excited state for a given type of complex can be rationalized on the basis of a change in the σ-donor strength of L, the magnitude of the variation may be larger than one might expect simply on the basis of a change in the energy of the (d,π^*) state. An interesting possibility is that two types of (d,π^*) CT states may be important, namely $(d\pi,e_g(\pi^*))$ and $(d_{xy},e_g(\pi^*))$. The energies of these two states may not necessarily vary in the same way with a change in the axial ligands. The energy of the d_{xy} orbital should be perturbed mainly inductively by a change in the electron density at the metal. The dπ energy should be similarly perturbed, as well as directly perturbed by π-backbonding. These two CT states could also have different inherent decay rates to the ground state, dependent, for example, on the relative magnitudes of the spin–orbit coupling in each complex.

Our analysis also gives a reasonable explanation for the observations on $RuTPP(Me_2SO)_2$, the lowest excited state of which we assign as $^3(\pi,\pi^*)$. As noted above, the relatively short lifetime (1.6 μs) may be due primarily to decay of $^3(\pi,\pi^*)$ via the close-lying (d,π^*) state (Figure 5A). That (d,π^*) is above $^3(\pi,\pi^*)$ in $RuTPP(Me_2SO)_2$ and below $^3(\pi,\pi^*)$ $RuTPP(py)_2$ and $RuTPP(pip)_2$ is consistent with both the weaker σ-donor strength of Me_2SO and its ability as a π-acceptor. In contrast, we have assigned (d,π^*) as the lowest excited state of the corresponding OEP complex, $RuOEP(Me_2SO)_2$ (Figure 5C). One possible reason for this difference is that $^3(\pi,\pi^*)$ probably is higher in energy in $RuOEP(Me_2SO)_2$ than it is in $RuTPP(Me_2SO)_2$. This view is based on phosphorescence data observed here for the RuP(CO)(L) complexes and previously[17] for other OEP versus TPP complexes.

An important question is why does a (d,π^*) CT state have a shorter lifetime than a ring $^3(\pi,\pi^*)$ state, even if the former may be at somewhat higher energy? A very likely reason is that larger (solvent plus internal) configurational changes probably accompany the decay of a metal-to-ring (d,π^*) CT excited state than those that accompany the decay of a ring $^3(\pi,\pi^*)$ excited state. This would result in a better Franck–Condon (vibrational overlap) factor for radiationless decay, to the ground state, of (d,π^*) as compared to $^3(\pi,\pi^*)$.

Photodissociation of the RuP(CO)(L) Complexes. The proposed thermally activated decay of $^3(\pi,\pi^*)$ via (d,π^*) in RuP(CO)(L) complexes also may be the photodissociative pathway. The quantum yield for the process $RuTPP(CO)(pip) \rightarrow RuTPP(pip)_2$ was found previously to be temperature dependent.[8] On the basis of this data it was postulated that the dissociative state is either a (d,π^*) CT or a ligand field (d,d) state lying in energy above, but thermally accessible from, $^3(\pi,\pi^*)$. In addition, to explain the excitation-wavelength dependence, it was suggested that a dissociative state might also lie in energy between the ring first (visible = Q) and the second (Soret = B) excited singlet state.[8] One might expect a $(d\pi,e_g(\pi^*))$ CT state to be dissociative with respect to CO, since removal of electron density from the filled metal dπ orbitals would decrease Ru(dπ) → CO(π^*) π-backbonding. Also, the added electron density in the normally empty ring $e_g(\pi^*)$ orbitals, in either (dπ,$e_g(\pi^*)$) or (d_{xy},$e_g(\pi^*)$) excited states, might weaken the bond to CO. A metal → axial-ligand (d,CO(π^*)) CT also might be dissociative, but it is expected to lie at too high an energy, based on the position of CO(π^*) in molecular orbital calculations.[5] The (d,d_{z^2}) ligand field excited state, which is dissociative for at least purely σ-bonded ligands (see ref 15), is probably at too high an energy to be thermally accessible from $^3(\pi,\pi^*)$; calculations place the empty d_{z^2} orbital substantially above dπ and d_{xy}.[5] However, (d,d_{z^2}) could lie in energy between the $^1(\pi,\pi^*)$ (Q) and Soret (B) states, with the (dπ,$e_g(\pi^*)$) between $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$. If so, the quantum yield for photodissociation with Soret-band excitation might be greater than with excitation in the Q bands, as was observed previously[8] for RuTPP(CO)(pip). However, as noted in Results, we did not observe such an effect for RuTPP(CO)(py). More studies on the possible wavelength dependence of the photodissociation yield would help to clarify this issue. Nonetheless, the proposal that a metal-to-ring (d,π^*) CT state is thermally accessible from $^3(\pi,\pi^*)$ in the RuP(CO)(L) complexes readily explains our time-resolved measurements and the photodissociation behavior of the compounds.

Acknowledgment. This work was supported by National Institutes of Health grant No. GM34685. We thank C. Kirmaier for valuable assistance with the picosecond measurements, J. Rodriguez for measuring the lifetimes of RuOEP(CO)(py) and RuOEP(CO)(pip) in 3-methylpentane, D. Dolphin and B. R. James for the initial samples of RuOEP(CO)(EtOH), RuOEP-(CO)(py), and RuOEP$(py)_2$, and M. Gouterman and A. W. Maverick for many helpful discussions.

Origin of Intramolecular Torques in ICN Photofragmentation

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Hamilton's equations are used to determine the importance of nearest-neighbor repulsive forces compared with bending forces in recent classical trajectory calculations of ICN or ClCN photofragment rotation.

Photodissociation of a triatomic molecule is sufficiently complicated that it is a challenge to determine which of the several sources of fragment rotation are most important for a particular molecule. Several recent classical trajectory (CT) calculations consider this question. Two sources of photofragment rotation have been discussed in these papers, and comparisons have been made between experimental results and the results of the calculations, to learn which influences are of greatest importance in determining the rotational state of the fragment. A dissociation fragment rotates either because some of its rotation as part of the parent molecule is preserved through the dissociation event, or because a torque acts on the fragment during the dissociation and the fragment is accelerated by this torque. We are concerned in this note with processes within the dissociating molecule which accelerate the rotation of the fragment, which are the bending forces that arise from the same sources that provide them in a stable molecule, and the short-range repulsive forces which act to repel the diatomic fragment and the atom, which are unique to a dissociating molecule. A bibliography of recent work in this area of photochemistry can be found in a recent paper from one of the most active groups.[1]

Origin of Fragment Rotation

It is generally accepted that the amount of rotation excited in CN from photodissociation of ICN (or ClCN) is determined by the conformation of the molecule in its ground state and in the excited state(s) reached in the absorption, and by the internal motions in the molecule in these states. Hess and Leone[2] have given a clear discussion of the several states involved in the photoabsorption by ICN.

To understand how the rotation of the fragment is generated during the dissociation it is natural to ask about the torques exerted on the fragment during the event; torques lead to increased angular velocities, and thus to increased angular momenta. In the general case, fragment rotation will be influenced by the motions of the parent molecule prior to dissociation. This note is not a thorough examination of all sources of rotation, but we mention in passing that, for ICN in particular, the rotation of the parent molecule is not an important source of fragment rotation.[3]

The two suggested sources of torque arising in the dissociation were described as upper state bending forces and nearest-neighbor repulsive forces. In any real molecule, both sources may be present in the dissociation; how important they are in any mathematical model of dissociation may be assessed by determining, at any point on the trajectory, how much torque can be assigned to each of the sources. The functional forms of the interaction potentials used in the various calculations differ and so do the expressions for the torque. We first apply Hamilton's equations to a Hamiltonian in which there is no upper-state bending force and show that nearest-neighbor repulsion leads to a torque on the CN. Then we examine the Hamiltonians used in recent studies of this problem, and show that, although these Hamiltonians contain an exponential repulsion term, with none of the Hamiltonians do we find a clearly identifiable torque arising from the repulsive forces. The authors whose work we study here probably did not intend that such a bias should be present in their analyses.

To complete this section we quote two brief excerpts from recent papers which have given especially concise descriptions of the physical bases of exciting rotation in photodissociation. From ref 4 we take the following description of the bending force mechanism: "...the high "temperature" in the fragment rotational distribution must be caused by the hill in the bending degree of freedom in the vicinity of the linear configuration". From ref 3 we take an apt description of the nearest-neighbor repulsion mechanism: "Final state interactions have also been proposed to be the cause of fragment rotational energy. For a triatomic dissociation ABC → A + BC, the simplest view would hold that the repulsion between A and B will cause rotation in the BC fragment as long as the line joining A and B does not also contain

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