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Picosecond Flash Photolysis of Carbonyl Complexes of Ruthenium(II) Porphyrin π Cation Radicals

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Abstract: With picosecond transient absorption techniques we have investigated photolysis of the Ru(II) octaethylporphyrin π cation radicals $\mathrm{Ru(OEP^{+}\cdot)CO(L)}$: L = EtOH (**4a**), py (**4b**), Im (**4c**), $\mathrm{Br^-}$ (**4d**). Excitation with 35-ps flashes at 532 nm results in the formation and decay of transient states having lifetimes less than the flash duration. The transient lifetimes for $^2A_{1u}$ ground-state π cation radicals are shorter than those observed after excitation of species with the $^2A_{2u}$ ground state. The transient behavior is rationalized in terms of both release of CO followed by rapid geminate recombination and of rapid radiationless decay via nondissociative states. The latter process seems more likely, but the former cannot be ruled out. Low-lying (d, π) charge-transfer states of the π cation radicals might provide effective routes for deactivation. Photolysis with 355-nm flashes results in the formation of similar short-lived transients. However, in the case of **4a** and **4b**, having mainly the $^2A_{2u}$ ground state, a longer-lived photoproduct is observed. This new transient could be the carbonyl-free π cation radical, but it is more likely the Ru(III) species obtained upon release of the CO followed by internal electron transfer from metal to ring. The quantum yield of the long-lived photoproduct appears to be low (<25%). Decarbonylation with 355-nm pump pulses is ascribed to the population of a dissociative state, such as (d_π, d_{z^2}), not accessible with the lower energy 532-nm excitation flashes. Apparently, rapid deactivation to the ground state competes favorably with ligand release even in these cases. The behavior is discussed in terms of the electronic states of the ring, metal, and ligands. The relevance of these findings to the release of ligands by hemoglobin and myoglobin as well as by other transition metal porphyrin complexes is considered.

Introduction

The transport of electrons in the respiratory chains of aerobic organisms involves, inter alia, the movement of electrons between cytochromes which are hemoproteins and function via an Fe(II) ⇄ Fe(III) couple. However, the way in which an electron moves from one iron atom to another is unknown. A currently favored hypothesis is that electrons are initially transferred via the porphyrin periphery, which acts as a conduit to the metal.[1] The transfer of electrons to and from a porphyrin macrocycle is a well-established phenomenon,[2] and the oxidation of a metalloporphyrin to generate the corresponding π cation radical plays a critical role in the enzymic functioning of catalase and horseradish peroxidase, and probably is similarly important in the enzymic reactions catalyzed by cytochrome–P450.[3]

The occurrence in nature of the peripheral redox chemistry of the porphyrin macrocycle led to the suggestion that electron transport in the cytochromes could be envisaged as proceeding similarly.[4] Thus the oxidation of ferrous cytochrome (**1**) to the ferric state (**3**) could be written as follows:

$$\underset{\mathbf{1}}{\mathrm{Fe^{II}(P)}} \xrightarrow{-e^-} \underset{\mathbf{2}}{\mathrm{Fe^{II}(P^{+}\cdot)}} \xrightarrow[\text{transfer}]{\text{internal}} \underset{\mathbf{3}}{[\mathrm{Fe^{III}(P)}]^+}$$

where P is the porphyrin macrocycle and **2** is a ferrous porphyrin π cation radical.

This hypothesis has no validity, of course, if **2** and **3** are simply resonance structures of the same ground state. However, the differences in ionic radius and axial ligation expected between a ferric and ferrous complex could allow for an energy barrier between **2** and **3** so that **2** could be a discrete intermediate. As yet, no such ferrous porphyrin π cation radicals have been reported with either cytochromes or simple iron porphyrins. Nevertheless, the electronic events **1** → **2** ⇄ **3** have been mimicked with a nickel porphyrin.[5]

We chose to use the second-row analogue ruthenium, which, being more kinetically inert than iron, might stabilize transient intermediates analogous to **2**. In fact, stable complexes analogous to both **1** and **2** can be prepared containing CO and an additional (sixth) ligand (L). Electrochemical studies have demonstrated that intramolecular electron transfer can occur upon change in ligation in the reaction:[6,7]

$$\underset{\mathbf{4}}{[\mathrm{Ru^{II}(OEP^{+}\cdot)(CO)L'}]^+} + 2\mathrm{L} \rightarrow [\mathrm{Ru^{III}(OEP)L_2}]^+ + \mathrm{CO} + \mathrm{L'}$$

case 1: (L′ = empty coordination site, L = $\mathrm{P(}n\mathrm{\text{-}Bu)_3}$ or $\mathrm{PPh_3}$)

case 2: (L′ = py or Br, L = $\mathrm{P(}n\mathrm{\text{-}Bu)_3}$ only)

($\mathrm{H_2OEP}$ = octaethylporphyrin)

We felt that alternative methods of removing the carbonyl from **4** might also promote internal electron transfer. In addition the π-back-bonding between the metal and the CO is expected to be weaker in the π cation radical than in the parent porphyrin, facilitating removal of the CO. Thus, studies of **4** might also be informative with regard to the binding and release of CO by the central Fe atom of hemoglobin and myoglobin. To these ends, we have examined the photolysis of the cation-radical species **4** using picosecond laser techniques to obtain the absorption spectra and the kinetic behavior of transient species formed upon excitation.

Another outstanding question is the relationship between biological function and the changes that occur in the electronic distribution in the porphyrin macrocycle during the course of a reaction. The highest filled molecular orbitals of metalloporphyrins

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are $a_{1u}(\pi)$ and $a_{2u}(\pi)$ in D_{4h} symmetry. The relative energies of these orbitals, and thus the one from which the electron will be removed upon oxidation, depends on the peripheral groups attached to the ring, the central metal, ligands, the counterions, and supporting electrolyte. The $^2A_{1u}$ and $^2A_{2u}$ ground-state π cation radicals have different electron density distributions as determined by ESR and exhibit different absorption spectra.[2,4] Unpaired spin density in the $^2A_{2u}$ ground-state π cation–radical resides mainly on the nitrogens and meso carbon atoms, while the $^2A_{1u}$ species has most of the unpaired spin density on the α-pyrollic carbons.[2] Thus, the different ground-state π cation radicals might be expected to have different affinities for ligands bound to the central metal. Therefore, we have examined the photolysis of **4** with various sixth ligands and under conditions where either or both the two types of π cation radicals are present in the ground state.

Experimental Section

Tetra-*n*-butylammonium perchlorate ($TBA^+ClO_4^-$) and carbonyl(ethanol)(octaethylporphyrinato)ruthenium(II) (**5**) were prepared as described previously.[7] The purification of solvents and the electrochemical preparation of the cation radical have also been described.[7] For the experiments described in the present paper, the electrochemical preparations (and picosecond measurements) were carried out in a flow cell described previously[8] and maintained under an inert Ar atmosphere. All other chemicals were reagent grade.

Carbonyl(octaethylporphyrinato)(pyridine)ruthenium(II) [Ru(OEP)(CO)(py) (6)]. This was prepared from **5** by a modification of a method reported earlier.[9] Complex **5**, 150 mg (0.20 mmol), was dissolved in dichloromethane (100 mL) with an excess of pyridine (1 mL) and refluxed for 1 h. The solid obtained after removing the solvent by evaporation was chromatographed on Activity III alumina (Merck neutral activ 90), using CH_2Cl_2 as eluent, and dried under vacuum, yield 126 mg (85%): ν(CO) 1933 cm^{-1}; optical spectrum (CH_2Cl_2: λ max, nm (log ϵ)), 396 (5.41), 518 (4.23) 549 (4.41); lit.[9] 396 (5.37), 518 (4.20) 549 (4.39). Anal. Calcd: C, 68.08; H, 6.67; N, 9.45. Found: C, 68.14; H, 6.60; N, 9.46.

Carbonyl(imidazole)(octaethylporphyrinato)ruthenium(II) [Ru(OEP)(CO)(Im) (7)]. The ethanol complex (**5**), 100 mg (0.14 mmol), and 14 mg (0.2 mmol) of imidazole were dissolved in CH_2Cl_2 (150 mL) and taken down to dryness on a rotary evaporator. The solid was chromatographed on Activity III alumina, eluted with CH_2Cl_2, and dried under vacuum, yield 77 mg (75%): ν(CO) 1933 cm^{-1}; optical spectrum (CH_2Cl_2: λ max, nm (log ϵ)); 396 (5.45), 518 (4.23), 550 (4.36). Anal. Calcd: C, 65.82; H, 6.63; N, 11.51. Found: C, 65.81; H, 6.42; N, 11.49.

For bulk photolysis a 500-W tungsten–halogen lamp was used. Typically a 1-cm cell containing the solution ($\sim 10^{-4}$ M) was placed inside a Liebig condenser with the flowed cooling water also acting as a filter for the infrared radiation. The solution in the cell was purged with argon via a Teflon or stainless steel needle while being irradiated by the lamp, at a distance of ~10 cm.

The dual-beam picosecond transient absorption spectrometer has been described in detail elsewhere.[10] A mode-locked Nd:YAG laser delivers single 35-ps, 1064-nm, 10-mJ pulses at 10 Hz. Radiation at 1064 nm is split into two parts by a beam splitter to drive the excitation (pump) and monitoring (probe) legs of the apparatus. Pump pulses at 532 nm (2 mJ) or 355 nm (300 μJ) are generated in KD*P crystals. The excitation radiation is focused to a 1- or 2-mm diameter spot in the center of the 1-mm pathlength flow cell containing the sample. The 1064-nm radiation in the probe leg of the apparatus traverses a variable-length delay line and is focused into a cell containing $CCl_4/CHCl_3$, to generate a weak, ~35-ps "white-light" probe flash that extends from 450 to 950 nm. Delay times in the range of minus several hundred picoseconds to about 10 ns can be obtained.

Results

Ground-State Absorption. As reported previously,[6,7] electrochemical oxidation of the complexes Ru(OEP)CO(L) (L = EtOH, py, Im) occurs reversibly at a potential of about +0.8 V (vs. Ag/AgCl(aq) electrode) in CH_2Cl_2 with TBA^+ClO_4- (0.05 M) as supporting electrolyte. The product formed by electrochemical oxidation of Ru(OEP)(CO), generated by dissolving Ru(OEP)CO(EtOH) (**5**) in CH_2Cl_2, has been shown, on the basis of ESR and optical spectral data,[2,7,11-13] to be a porphyrin π cation radical with a $^2A_{2u}$ ground state (Figure 1A). Coordination of axial ligands such as py, $(CH_3)_2SO$, or 4-Me(py) to the $^2A_{2u}$ ground state species has little effect on the spectrum of the cation radical. For example, Ru(OEP$^{+}\cdot$)CO(CH_3CN) (Figure 1B), prepared by electrolyzing **5** in CH_3CN, has a very similar spectrum to the ethanol adduct. On the other hand, chemical oxidation of **5** in CH_2Cl_2 using a dilute solution of bromine gives a product with a dramatically different optical spectrum (Figure 1C). The

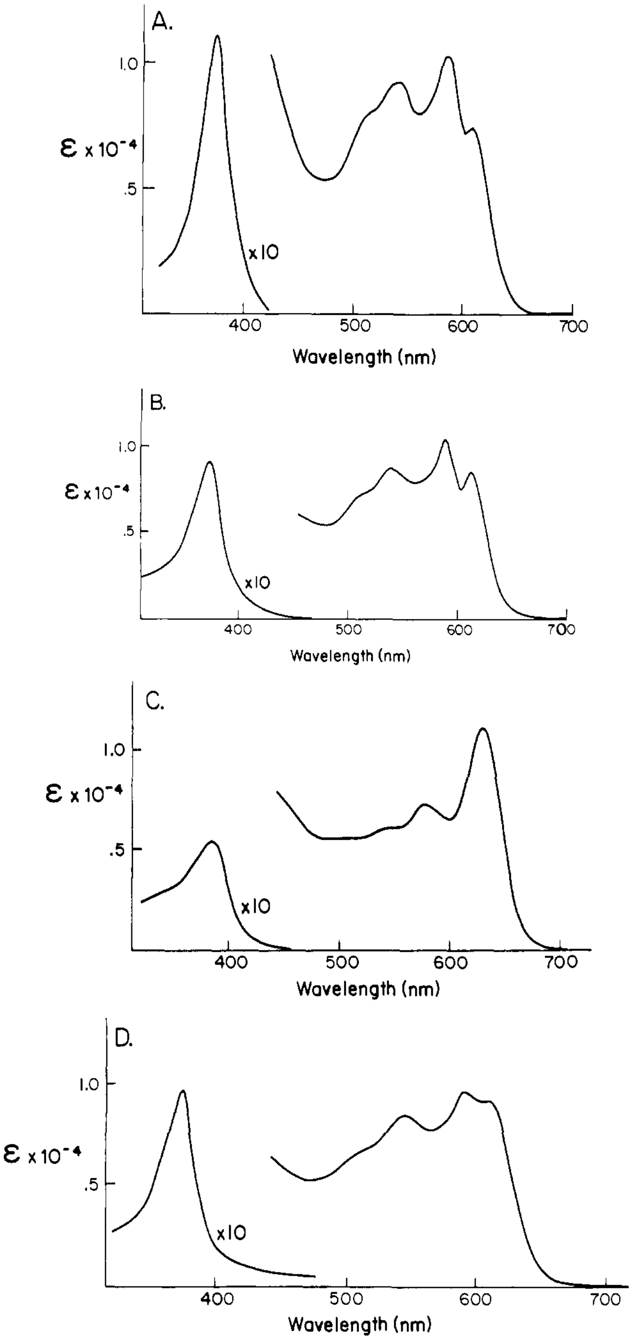

Figure 1. Optical absorption spectra of the cation–radical species Ru(OEP$^{+}\cdot$)CO(L), studied. See Table I for identifications. (A) L = EtOH; species with L = py has an almost identical spectrum; (B) L = MeCN; (C) L = Br^-; (D) L = Im. Note that the wavelength scales are different for each panel. The strong near-ultraviolet Soret band should be multiplied × 10.

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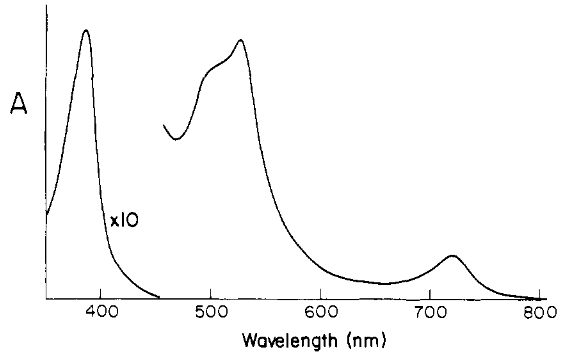

Figure 2. Optical absorption spectrum of the product obtained by bulk photolysis of Ru(OEP$^{+}\cdot$)CO(py) (after purification). The spectrum is consistent with a Ru^{III}OEP species.[6,7]

spectroscopic properties of this species are consistent with a π cation radical having a $^2A_{1u}$ ground state.[7] Other axially coordinated ligands, such as Im (Figure 1D), result in spectra of the oxidized species that appear to be a more equal mixture of the $^2A_{2u}$ and $^2A_{1u}$ ground-state radicals.

It is possible that the axial ligand modifies the spectrum of the appropriate ground state by the mixing of ligand and porphyrin orbitals, or through porphyrin–ligand charge-transfer transitions.[9] However, considering the effects of ligands discussed here, it is more likely that the spectral changes seen in Figure 1A to 1D are due to a thermal mixture of the two ground states in proportions depending upon the nature of the axial ligand. Therefore, we consider the EtOH (**4a**) and py (**4b**) complexes of Ru(OEP$^{+}\cdot$)(CO) to possess mainly $^2A_{2u}$ character, the Br$^-$ complex (**4d**) to have mainly $^2A_{1u}$ character, and the Im complex (**4c**) to be a mixture of the two ground states.

Photolysis of Ru(OEP$^{+}\cdot$)CO(py) (4b). Bulk photolysis of a solution of **4b** ($\sim 2.5 \times 10^{-4}$ M) for ~40–50 min with a tungsten–halogen lamp (see Experimental Section) gave a deep orange solution whose spectrum showed an increased absorption in the 490–540-nm range and a loss of 540-, 587-, and 610-nm peaks characteristic of the original $^2A_{2u}$ cation radical. Chromatography on a silica gel column allowed separation of an orange band (Figure 2) from other unidentified products responsible for most of the absorption above ~560 nm in the photolyzed sample. Although the orange product was not characterized, the visible spectrum is very similar to those of other Ru(III) porphyrin complexes,[7] strongly suggesting that intramolecular electron transfer has occurred from the metal to the porphyrin.

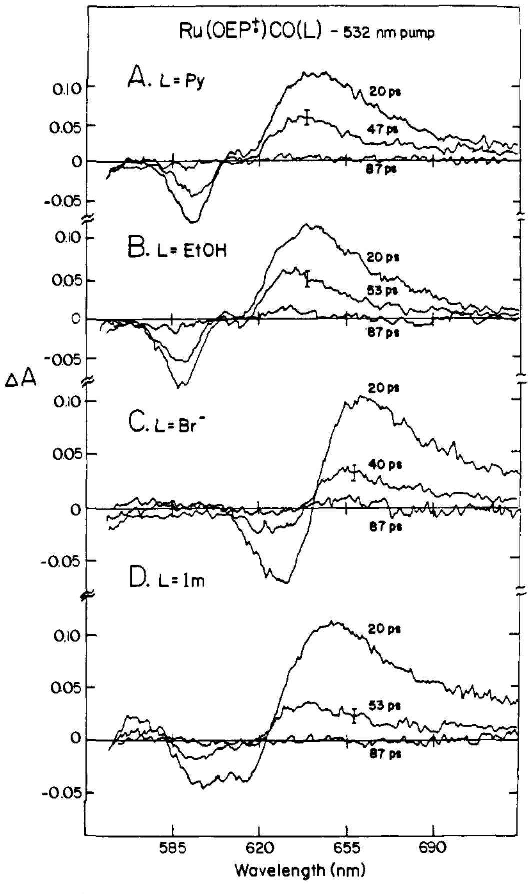

Figure 3. Difference spectra obtained at several delays following excitation of Ru(OEP$^{+}\cdot$)CO(L) with 532 nm flashes. (A) L = py; (B) L = EtOH; (C) L = Br$^-$; (D) L = Im. Each spectrum represents the average of approximately 300 spectra, with standard deviations in ΔA of ≤ 0.01 over the wavelength region shown as indicated by the error bars.

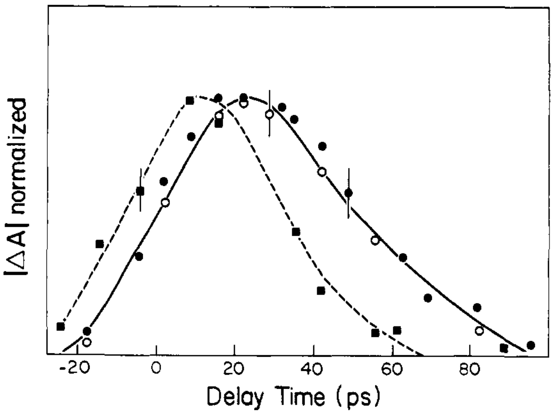

Figure 4. Time evolution of the excited-state absorption produced by excitation with 35-ps flashes at 532 nm. The probe wavelengths are 635 nm for L = py (**4b**) (●) or L = EtOH (**4a**) (○), and 655 nm for L = Br$^-$ (**4d**) (■). The solid curve is a computer fit for the convolution of the 35-ps flashes with a transient having a 25-ps lifetime. The dashed curve shows a similar fit, but for a transient with a 10-ps lifetime. Although the curves fit the data well, care must be taken on extracting accurate lifetimes from such a procedure. Here we are more interested in deducing trends in the transient lifetimes with the type of π cation–radical ground state (Table I). The absorption changes have been normalized to the maximum values at the probe wavelength.

Flash photolysis of **4b** with saturating 35-ps, 532-nm excitation pulses gave rise to a short-lived intermediate whose difference spectrum at several delays is shown in Figure 3A. The spectrum of this transient exhibits strong new absorption with a maximum near 635 nm and bleaching in the ground-state absorption bands between 575 and 610 nm (cf. Figure 1A). The time evolution of the transient absorption increase at 635 nm is shown in Figure 4A (filled circles). Analysis of this time profile indicates that it can be fit reasonably as the convolution of the 35-ps pulse profiles and a transient decay with a 20–30-ps time constant.[14] Preliminary measurements on **4b** with 8-ps, 530-nm excitation flashes from a mode-locked Nd:glass laser system yielded a transient absorption spectrum at a 20-ps delay that was the same within experimental error as that shown in Figure 3A, and the decay time of the transient was measured to be 22 ± 5 ps. This agrees well with the value of 20–30 ps estimated from the kinetic behavior shown in Figure 4. Thus, the transient absorption spectrum resulting from photolysis of **4b** with 532-nm flashes has disappeared completely by 87 ps and no longer lived products were detected (Figure 3A). These experiments suggest that the transient species returns rapidly to the ground-state cation radical, and, if the CO is released and the Ru(III) product forms, it does so

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(14) It is always difficult to deconvolute an accurate lifetime for a transient on the same order as or less than the pulse duration. Such a procedure is especially difficult when strong flashes are required and systems such as those investigated here, where there is the distinct possibility of the rapid turnover of more than one short-lived intermediate during the flash. The time profiles and estimated transient decay times were quite reproducible and definite trends were observed (Table I). As discussed in the text, this procedure appears to give good approximations for lifetimes in the 10–30-ps range, judging from comparison with measurements on **4b** made with shorter duration flashes. The convolution integral is discussed by: Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500–2506.

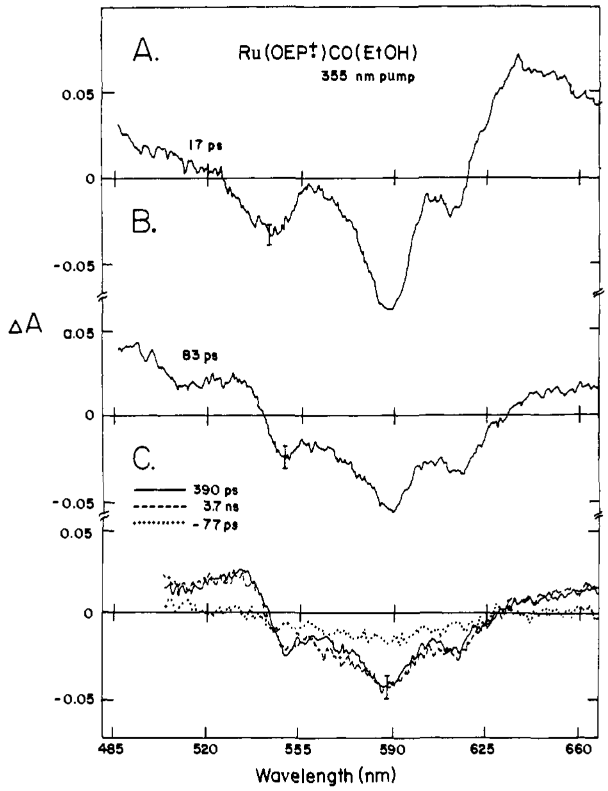

Figure 5. Differences spectra as a function of delay time following excitation of Ru(OEP$^+$·)CO(EtOH) with 355-nm flashes: (A) 17 ps; (B) 83 ps; (C) 390 ps (—), 3.7 ns (- - -), -77 ps (···). The spectra in (A) and (B) were taken over two wavelength intervals and are shown as continuous, as they overlapped very well in the large region common to the two. The small bleaching at the negative delay in (C) is probably caused by some long-lived product not swept out the excited region by the flow system between laser shots.

in very low quantum yield. However, the cumulative effect of a large number of laser pulses (several thousand) did cause a permanent change in the ground-state spectrum consistent with some Ru(III) formation. This observation is in agreement with the results of the bulk photolysis experiments described above.

Excitation of **4b** with 355-nm flashes resulted in the formation of a long-lived photoproduct, the spectroscopic behavior of which will be discussed below along with similar measurements on the ethanol complex (**4a**).

Photolysis of Ru(OEP$^+$·)(CO)EtOH (4a). The results for flash photolysis of **4a** at 532 nm are nearly identical with those just discussed in detail for the py complex **4b**. Both cation radicals have the $^2A_{2u}$ ground state. The ground-state absorption spectrum (Figure 1A), the transient difference spectra (Figure 3B), and the decay kinetics of 20–30 ps (Figure 4A, open circles) for **4a** are all similar to those just presented for **4b**.

However, in contrast to the pyridine complex **4b**, bulk photolysis of **4a** for a few minutes gave unidentified products whose spectrum showed continuous and featureless absorption extending to ~800 nm. The lack of a ligand capable of stabilizing the product of intramolecular electron transfer apparently caused degradation reactions to predominate. However, it is possible that some Ru(III) species were formed here, as in the case of **4b**.

Excitation of **4a** or **4b** with 355-nm flashes gave rise to the transient behavior shown for **4a** in Figure 5. The spectra during and shortly after the flash (panel A) are similar to those obtained with 532-nm excitation flashes (Figure 3A and B), in the common wavelength region. The transient absorption to the red of 610-nm decays with a time constant of 20–30 ps as occurs with 532-nm flashes (Figure 4A circles). However, there is a long-lived state, as evidenced by the residual bleaching in the 540–625-nm region and weak absorption to the red and blue. This state has a lifetime of >5 ns, judging from the virtually identical spectra at 390-ps and 3.7-ns delays in Figure 5C. Figure 5C also shows a spectrum at a negative delay (dotted curve) that should have $\Delta A = 0$, but shows some bleaching in the 540- to 610-nm region. We attribute this to some of the long-lived photoproduct that was not swept out of the exited region between flashes by our anaerobic flow system. Considering the 10-Hz repetition rate, this means that the long-lived product actually has a lifetime of 100 ms or longer. Taking this into account and comparing with the other spectra in Figure 5, we estimate an upper limit of 25% for the quantum yield for the formation of the long-lived transient upon photolysis of **4a** or **4b** with 355-nm flashes.

Table I. Summary of Results on Ru(OEP$^+$·)CO(L)

L	compd	ground state[a]	transient lifetime,[b] ps	long-lived state[c]
EtOH	4a	$^2A_{2u}$	20–30	yes
py	4b	$^2A_{2u}$	20–30	yes
Im	4c	$^2A_{2u} + {}^2A_{1u}$	15–25	no
Br$^-$	4d	$^2A_{1u}$	≤15	

[a] Major ground-state species judging from the optical spectra of Figure 1. [b] Lifetime estimated from analysis of the time behavior of the absorption changes with 532- and 355-nm photolysis pulses (cf. Figure 4), assuming the convolution of 35-ps flashes with a single transient having an exponential decay. [c] Long-lived state having a lifetime >5 ns (≥100 ms) observed with 355-nm flashes.

Photolysis of Ru(OEP$^+$·)CO(Br$^-$) (4d). Compound **4d** has an $^2A_{1u}$ ground state and a spectrum (Figure 1C) that is red-shifted from that of the $^2A_{2u}$ ground-state π cation radicals **4a** and **4b**. The transient difference spectrum resulting from photolysis of **4d** with 532-nm flashes (Figure 3C) shows bleaching in the ground-state bands with a maximum bleaching near ~630 nm, and strong new absorption to the red with a peak near 660 nm. Analysis of the time profile of the transient absorption (Figure 4, squares) indicates that the lifetime is <15 ps, shorter than that of 20–30 ps estimated for compounds **4a** and **4b** (Figure 4, circles). The transient spectrum produced by 532-nm flashes has disappeared by 87 ps, and no long-lived state was observed (Figure 3C). Sample **4d** was much less stable than **4a** or **4b**. The permanent effect of the photolysis was partial reduction of the sample, which could be regenerated by the addition of more bromine. Because of this instability and the presence of bromine, we did not attempt experiments with 355-nm flashes.

Photolysis of Ru(OEP$^+$·)CO(Im) (4c). The ground-state absorption spectrum (Figure 1D) indicates that Ru(OEP$^+$·)CO(Im) (**4c**) contains a mixture of the $^2A_{1u}$ and $^2A_{2u}$ configurations. Photolysis of **4c** with 532-nm pulses gave rise to the difference spectrum shown at several delays in Figure 3D. Comparison with the corresponding spectra for **4a**, **4b**, and **4d** (Figures 3A–C) supports the contention that the Im complex contains a mixture of the two π cation–radical ground-state configurations. The transient lifetime for **4c** appears to be intermediate between that for **4a** or **4b** and that for **4d** (Table I). Photolysis of **4c** with 355-nm flashes gave rise to a difference spectrum essentially the same as that obtained with 532-nm excitation pulses (Figure 3D). However, unlike **4a** and **4b**, both the transient absorption and the bleaching in the 480–720-nm region for **4c** recovered with a 15–25-ps time constant. No longer lived product was detected.

Spectra of the Transient States. Figure 6 compares the ground-state spectra for π cation radicals **4a**, **4b**, and **4d** with absorption spectra of the corresponding transient states. These absorption spectra were calculated from the difference spectra of Figure 3 and the ground-state spectra, assuming that 85% of the ground-state molecules were converted to the transient state during the 532-nm excitation flash. This value is reasonable upon considering the overlap of the pump and probe pulses at the sample and measurements with the pump-pulse intensity reduced. The important point to be drawn from these comparisons is that the transient spectra have their absorption maxima red-shifted from the maxima in the corresponding ground-state spectra, but still have substantial absorption at the same wavelengths as the ground state. In fact, the transient state for the $^2A_{2u}$ π cation radical (dashed curve in Figure 6A) has a spectrum very similar to the

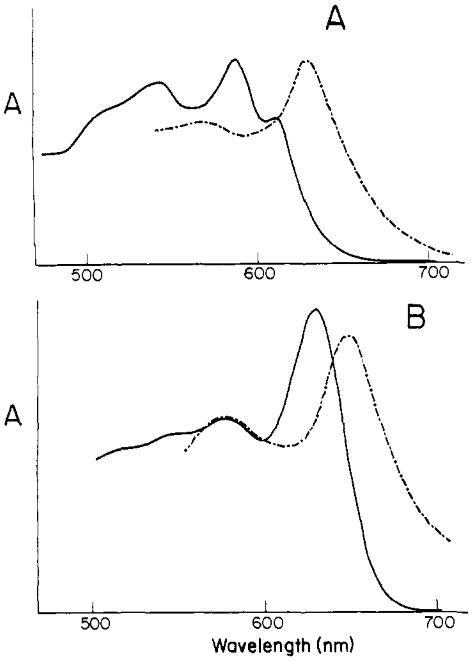

Figure 6. (A) Spectrum of the $^2A_{2u}$ ground-state species **4a** and **4b** (—) and the intermediate (···) formed on photoxidation. (B) Spectrum of the $^2A_{1u}$ ground-state species **4d** (—) and its corresponding transient intermediate (···). The spectra of the transient intermediates were estimated from the observed difference spectra (Figure 3) and the ground-state spectra (Figure 1), assuming that 85% of the molecules in the excited region were converted to the transient state by the excitation flash.

ground state of the $^2A_{1u}$ π cation radical (solid curve in Figure 6B). These observations suggest that the transitions giving rise to the transient spectra are very similar to, or the same as, the π-π^* transitions responsible for the ground-state spectra.

Discussion

Some general results from the picosecond flash photolysis measurements on the Ru(II) porphyrin π radicals (**4a**–**4d**) are gathered together in Table I. We first consider reasons for the rapid decay times and lack of a detectable long-lived component following excitation with 532-nm flashes.

Low yields for photodissociation of MbO_2 and HbO_2 (~3%) are observed with long-duration photolysis pulses or continuous illumination.[15–19] However, a number of subnanosecond-resolution transient-absorption[20–25] and resonance Raman[26–28] studies have been carried out to explain the high photodissociation yields of MbCO (50%) and HbCO (100%). Two possibilities have been considered for the low photodissociation yields of the oxy complexes. The first involves rapid energy relaxation in the initially excited complex, which competes favorably with dissociation. The second is rapid recombination of O_2 and heme before they can diffuse apart (geminate recombination). The nature of the initial excited state has also been of interest. Although there is not a complete consensus on this point, much of the evidence suggests that the low yield for photodissociation of O_2 from Hb and Mb is due mainly to fast relaxation of nondissociative states on a time scale of <15 ps.[20–25] On the basis of earlier spectroscopic work and iterative extended Hückel calculations,[29–31] it has been suggested[20,25] that the radiationless decay proceeds through low-lying charge-transfer (CT) states that are weakly or nondissociative. Recent INDO-SCF calculations support this view.[32] These CT states involve promotion of iron d electrons between molecular orbitals composed mainly of iron d and oxygen π_g orbitals.[30–32] The high density of these low-lying CT states may also facilitate rapid relaxation to the ground state. For the CO complex, on the other hand, the lowest excited states appear to be a (d_π, d_{z^2}) triplet ($^3T_1$) and a (d, d) quintet ($^5T_2$).[20,30,32] Such (d, d) states may be dissociative, because electron promotion to the d_{z^2} orbital will weaken the Fe–CO bond. Recent INDO-SCF calculations[32] suggest that the dissociative state is most likely the (d_π, d_{z^2}), as postulated previously.[31a] Release of CO from the singlet or triplet form of this (d, d) would be followed by conversion of the configuration on the metal to the $^5T_2$ ground state of the deoxyheme.[20,32] All of these studies suggest that dissociation mainly occurs from a (d, d) state below the porphyrin lowest (π, π^*) excited state.

Recent picosecond studies of ligated Co(II)[33,34] and Cu(II)[35,36] porphyrins support the view that low-lying CT states give rise to rapid radiationless decay, while ligands are readily lost following excitation of ligated Co(III)[34] and Ni(II)[37,38] porphyrins, where the lowest states are (d, d).

Similar ideas have been considered to explain the quantum yields obtained from the photodissociation of a number of diatomic and pseudodiatomic ligands from metalloporphyrin complexes [M(porph); M = Fe, Mn, and Co].[15] It was concluded that systems which could be considered formally d^6 around the metal atom (e.g., Fe^{II} + CO, Fe^{III} + NO, Mn^{II} + NO) gave a quantum yield of ~1, whereas systems formally with a larger number of electrons showed a lower quantum yield (e.g., Fe^{II} + NO, $\phi \sim 10^{-3}$; and Fe^{II} + O_2, $\phi \sim 10^{-4}$). In the latter cases it was argued that a low-lying CT state would lead to rapid deactivation competing with ligand release from higher energy states.[15]

The "d^6 rules" just described[15] do not appear to hold for CO complexes of the Ru(II) porphyrins, where the quantum yields for the displacement of the CO are generally very low.[39–42] This

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has been attributed in part to the CO being much more tightly bound to Ru(II) than to Fe(II).[39-42] However, if the difference in bond strengths is a major factor, then the formation of a Ru(II)–porphyrin π cation radical, which is expected to decrease backbonding from the metal to the carbonyl group, should cause a substantial increase in the quantum yield due to the weakening of the Ru–CO bond. Although the quantum yields for the photolysis of the cation radicals **4a–d** could not be measured here, the experimental results demonstrate that ϕ was low, even in cases where some long-lived or permanent photoproduct was observed. This implies that the deviation of Ru complexes, both neutral and cation radicals, from the "d^6" trends noted above is not due solely to the strength of binding of the carbonyl. However, iterative extended Hückel (IEH) calculations on a number of metalloporphyrin complexes indicate that the lowest excited states are a function of the metal, ligands, and macrocycle, not simply the electron count.[9,29] Thus, there may be no low-lying dissociative states in the Ru complexes.

Recent IEH calculations on Fe^{II}(OEP)CO(py) predict low-lying (d, d) transitions, such as (d_π, d_{z^2}), that are observed in near-IR absorption and that act to quench emission.[9] These states are similar to those discussed above for HbCO and MbCO and probably would be dissociative with respect to CO bound to the metal. On the other hand, for Ru(OEP)CO(py) the IEH calculations predict the (d, d) states and any (d, π^*) CT states to be higher in energy than the lowest porphyrin (π, π^*) excited states. Thus, normal porphyrin $\pi^* \rightarrow \pi$ phosphorescence is observed at 77 K,[9] although there is evidence that another state may be thermally accessible from the $^3(\pi,\pi^*)$ at room temperature.[41] Therefore, the calculations indicate that a low photodissociation yield for Ru(OEP)CO(py) might be expected, because there are no low-lying states which would be dissociative in character. This analysis is consistent with the low yield for CO release observed for several Ru–porphyrin CO complexes, including π cation radicals.[39-42]

Extension of these concepts to the Ru(OEP$^{+}\cdot$)CO(L) π cation radicals studied here suggests that photorelease of the CO by these species might have a low quantum yield for two reasons. One is the absence of low-lying dissociative (d, d) or [$a_{1u}(\pi)$ or $a_{2u}(\pi)$, d] CT states below the lowest porphyrin (π, π^*) excited state. Examples of photolabile states include those in which an electron has been promoted to the Ru d_{z^2} orbital, weakening the Ru–CO bond. To a first approximation, if there are no low-lying (d, d) or (π, d) states below the lowest (π, π^*) excited states in the neutral parent compounds,[9,29] then the same situation should probably exist for the π cation radicals and the yields for CO release might be expected to be low. Second, rapid relaxation competing with dissociation might be enhanced in the π cation radicals by the presence of low-lying (d, π) CT transitions not present in the neutral parent compounds. One electron is removed from either the porphyrin normally highest filled $a_{1u}(\pi)$ or $a_{2u}(\pi)$ orbitals to make the π cation radical. If the filled metal orbitals are not too far below the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ in energy, as appears to be the case for Ru(OEP)CO(py),[9] then there should exist low-lying transitions, filled-d_{xy} or -$d_\pi \rightarrow a_{1u}(\pi)$, $a_{2u}(\pi)$. With the opposite ordering, low-lying $\pi \rightarrow$ d "hole" transitions should be present. The (d, π) CT states arising from these transitions would be expected to provide effective pathways for deactivation in the porphyrin π cation radicals, in a manner similar to that discussed above for HbO$_2$, MbO$_2$, and ligated metalloporphyrins.

The lack of low-lying dissociative states for the Ru(OEP$^{+}\cdot$)-CO(L) species (**4a–d**) suggests that the short-lived transients we observe upon excitation with 532-nm flashes (Figures 3 and 6) are probably excited states of the π cation radicals with the CO still attached. As there has been essentially no work done on the excited-state spectra or kinetics of porphyrin π cation radicals, we do not have available comparative spectra to assign those we observed. Comparison of Figures 6A and 6B suggests that in the case of the molecules with a $^2A_{2u}$ ground state, the transient absorption spectrum is due to a $^2A_{1u}$ excited state, probably formed via relaxation of a [d, $a_{2u}(\pi)$] CT state. For Ru(OEP$^{+}\cdot$)CO(Br$^-$), with a $^2A_{1u}$ ground state, the transient spectrum looks more like a shifting of the $^2A_{1u}$ spectrum to the red. Perhaps the latter transient spectrum represents a photorelease of the Br$^-$ ligand; this would mean that the relaxation proceeds through a state, such as one of the low-lying (d, π) CT, that is nondissociative with respect to CO, but dissociative with respect to Br$^-$. Another possibility is that the excited $^2A_{1u}$ cation radical relaxes via a different one of the possible low-lying (d, π) CT states than does the excited $^2A_{2u}$ species, and that the transient spectrum in the $^2A_{1u}$ case is the CT. The different relaxation times for the $^2A_{2u}$ and $^2A_{1u}$ radicals could be explained as the former representing the relaxation $^2A_{1u} \rightarrow {}^2A_{2u}$, and the latter representing either a geminate recombination Ru(OEP$^{+}\cdot$)CO + Br$^-$ in Ru(OEP)$^{+}\cdot$)-CO(Br$^-$) or relaxation of a low-lying CT with both ligands attached.

The long-lived transients (Figure 5C) observed for **4a** and **4b** when the higher energy 355-nm photolysis pulses are employed could be either the decarbonylated Ru(II) cation radical or the Ru(III) product. The spectrum shown in Figure 5C is more consistent with the latter than the former, but the formation of the Ru(III) species would still involve release of CO as discussed in the Introduction. This is consistent with the fact that release of CO would probably make [Ru^{III}(OEP)]$^+$ lower in energy than Ru^{II}(OEP$^{+}\cdot$).[43] Dissociative (d, d) or (π, d) states not accessible with 532-nm photons might be reached with the 355-nm radiation. The IEH calculations[9] suggest that this might be the case, although better estimates of the energies of the various states are needed before the possibility of wavelength-dependent photochemistry can be predicted with more certainty. The release of the CO from these higher energy states would have to compete with radiationless decay through the relatively dense upper manifold of states nearby in energy, and then through the proposed lower energy (d, π) CT states.

It should be mentioned that we cannot rule out the possibility that, with either 532- or 355-nm flashes, a second photon could be absorbed by one of the excited species. Picosecond experiments on Hb complexes[20,25] revealed some broadened spectra at early delays that were discussed in terms of absorption of a second photon during the intense flash by short-lived states.[20,25] It is possible that absorption of a second 355-nm photon could lead to population of a dissociative state not accessible to absorption of one or two 532-nm photons. However, even in these cases the discussion given above on the nature of the dissociative states and relaxation pathways should apply.

Therefore, we tentatively view the long-lived product obtained upon photolysis of **4a** and **4b** as reflecting the Ru(III) product obtained upon decarbonylation accompanied by internal electron transfer. That no long-lived product was detectable upon photolysis of the Im cation–radical complex (**4c**) with 355-nm flashes suggests that the transients observed for the EtOH and py complexes are not simply due to an impurity or a degradation product formed in low yield. One possibility for this difference in behavior is that CT transitions involving the Im ligand act to deactivate the higher energy dissociative (d, d) states, and that similar states are not present or are not as effective with the py ligand (cation radical **4b**). However, preliminary analysis of the IEH calculations[9] indicates that this argument is speculative at best. Another view is that the CO is more tightly bound to the Ru in **4c** (and probably in **4d** also) than in **4a** or **4b**. Possibly, low-lying (d, $a_{1u}(\pi)$) CT states are more effective quenchers than those of the type (d, $a_{2u}(\pi)$). Still another possibility is that the dissociative state (d_π, d_{z^2}) has moved to an even higher energy in the Im complex and cannot be reached even with the 355-nm photons.[43] Thus, the transient absorption (Table I) decays faster for the mainly $^2A_{1u}$ ground-state π cation radical **4d**, and appears to be so as well for the Im complex **4c**, than for the mainly $^2A_{2u}$ ground-state species **4a** and **4b**, competing with ligand release. More extensive studies are needed on the quantum yields for the

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photodissociation of various ligands from porphyrin π cation radicals having the two different types of ground states before these possibilities can be distinguished.

Conclusions

Excitation of the Ru(II) porphyrin π cation radicals, Ru(OEP$^{+}\cdot$)CO(L), with 35-ps 532-nm flashes results in the formation of transient states that decay in <35 ps. There appears to be a correlation between the time constant for the decay and the type of π cation–radical ground state, a <15-ps transient for a $^2A_{1u}$ ground state and an ~25-ps transient for a $^2A_{2u}$ ground state. The kinetic behavior could reflect either decarbonylation followed by geminate recombination or else rapid relaxation via nondissociative states. Analysis of the results indicates that the latter is more likely, but that the former is responsible for at least part of the observed transient behavior cannot be ruled out. The spectra of the transient states suggest that the excited $^2A_{2u}$ ground-state π cation radicals might decay through an $^2A_{1u}$ excited state, while the decay of the excited $^2A_{1u}$ ground-state species with L = Br^- may involve either release and geminate recombination of the Br^- ligand or relaxation of a low-lying CT state with both ligands attached. It is suggested that rapid relaxation to the ground state in all these cases might be enhanced by low-lying (d, π) CT states. In fact, such CT states would tend to make the yield for release of CO from porphyrin π cation radicals lower than from the neutral parent compounds.

Excitation with 355-nm flashes also results in the production of short-lived transients. However, in the cases of the $^2A_{2u}$ ground-state π cation radicals (L = EtOH or py), a long-lived photoproduct is observed, which is ascribed to population of a dissociative state, such as (d_π, d_{z^2}), not accessible with the lower energy 532-nm excitation flashes. The yield is estimated to be <25%. This species is more likely the Ru(III) product obtained upon decarbonylation followed by internal electron transfer than the decarbonylated cation radical itself. This new species appears not to be a degradation product, as a long-lived state is not observed upon photolysis of the cation radical with L = Im, in which the ground state is a mixture of the $^2A_{2u}$ and $^2A_{1u}$. Several reasons for this difference in behavior have been considered, including a more tightly bound CO, more effective low-lying quenching states, and movement of the dissociative state to higher energy in the species having the $^2A_{1u}$ ground state. The relevance of our findings to photodissociation in hemoglobin, myoglobin, and simple metalloporphyrin complexes has been discussed.

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Spectral Shifts upon Reversible Modifications of CHO Peripheral Substituents in Porphyrin, Chlorin, and Bacteriochlorin. A Phenomenological Explanation for the Red Shift of Protonated Schiff Base

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Abstract: Previously, we have demonstrated that the formation of a protonated Schiff base metalloporphyrin resulted in a 50-nm red shift of the long wavelength absorption band relative to the unprotonated imine [*J. Am. Chem. Soc.* **1983**, *105*, 634.] A systematic study is now presented on the spectral properties of five formylporphyrin, chlorin, and bacteriochlorin systems upon formation of their protonated Schiff bases. The compounds used in this study were nickel complexes of 4-vinyl-8-formyl, 1,4-diformyl, and 4,8-diformyl derivatives of an alkyl porphyrin; copper 2,6-di-*n*-pentyl-4-vinyl-7-hydroxy-8-acroleinyl-1,3,5,7-tetramethylchlorin; and copper 2,6-di-*n*-pentyl-3,7-dihydroxy-4,8-diacroleinyl-1,3,5,7-tetramethylbacteriochlorin. In addition, pyrrolidine adducts as well as the neutral, but electron deficient condensates of malononitrile and ethyl cyanoacetate were also examined. It was concluded that the unusual red shift of absorption maxima in the visible region and the splitting/broadening of the Soret peak observed in protonated Schiff base porphyrin, chlorin, and bacteriochlorin are attributable to the resonance effect of a strong electron-withdrawing group. Studies of solvent and counterion effects further indicated that the conversion of a carbonyl to a Schiff base peripheral group would subject the spectral and redox properties of chlorin and porphyrin to a greater extent of environmental control. These results suggest that a Schiff base chlorophyll could be an attractive model for the photosynthetic reaction centers.

In many naturally occurring porphyrinoid compounds which contain ketone and/or formyl functional groups, e.g., chlorophylls in photosynthetic apparatii and heme *a* in cytochrome oxidase, it is often observed that the spectral properties of the in vivo and in vitro chromophores do not match.[1,2] This is particularly prevalent for the chlorophylls; for example, the visible absorption band of the chlorophyll reaction center P700 is red shifted relative to chlorophyll *a* (668 nm).[1] Several model studies suggest that P700 is a "special pair" dimer of Chl *a*.[1,3] However, this dimer

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