of oscillations. The computer shows that the skeleton mechanism requires approximately the increase of R_{O_2} with $[IO_3^-]$ that is reflected in the κ's of Table I. As proof, compare with these κ's the following computed values of κ and those in column 10, Table II. These are for $[IO_3^-]_0 = 0.3$ (as opposed to 0.1063) and $[H^+]_0$ and $[H_2O_2]_0$ unchanged.

t, min	1	3	5	7	9	11
$10^2 k$	0.304	0.789	1.202	1.415	1.734	1.876

t, min	14	20	40	100	200	260
$10^2 k$	1.987	2.01	1.719	1.186	0.820	0.703

At $[IO_3^-]_0 = 0.3$, the "Dushman reversal", previously mentioned, occurs between 3 and 4 min—earlier than in F-16.

The agreement of the k's above with the κ's of Table I is all that could be expected, for the κ's are average values. The increased R_{O_2} values following upon $[IO_3^-]_0$ increases exceed what can be directly accounted for by the rates of reactions in which IO_3^- is consumed. The R_{O_2} increases result because the entire reaction system readjusts itself to increasing $[IO_3^-]_0$, and it is gratifying that the skeleton mechanism provides for this readjustment.

The Skeleton Mechanism Today. This mechanism was designed to be revised as the examination of progressively more complex experimental material proceeds. It has yielded a surprisingly good *quantitative* description of the smooth catalysis as recorded in Table I—a description that included the *rates* of H_2O_2 decom-

position, which are the most important single measure of the catalysis. However, such success does not prove mechanism; for, as long hours at the computer have shown, many combinations of the assignable and interdependent specific rates can yield plausible descriptions.

Questions Remain. Why (see Table II) are initial computed R_{O_2} values greater than those measured? Supersaturation (preceded by saturation and N_2 displacement) may not be the whole answer. Why was it best to use $k_{2f} = 7.2$ min^{-1} (its maximum measurable value) here when 3 times that value was preferable in part 6? The skeleton mechanism may have to be modified by the addition of free-radical reactions, which would take it closer to that used by Edelson and Noyes[12] to simulate oscillations and move it further from that with which a similar result was achieved on a molecular basis.[19]

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Redox Properties of Metalloporphyrin Excited States, Lifetimes, and Related Properties of a Series of Para-Substituted Tetraphenylporphine Carbonyl Complexes of Ruthenium(II)

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Abstract: Excited-state and redox properties of Ru(p-XTPP)(CO), X = MeO, Me, H, F, Cl, H and Br, have been defined. Emission bands were centered at 730 ± 3 nm and excited-state lifetimes were in the range of 30 ± 10 μs. Two one-electron oxidations in CH_2Cl_2 ranged from 0.74 to 0.86 V for the first step and from 1.18 to 1.27 V for the second one. A one-electron reduction process in $(CH_3)_2SO$ ranged from −1.35 to −1.24 V. Excited-state lifetimes and redox potentials exhibit a weak dependence on the Hammett σ_p function. In general, redox potentials increase as the electron-withdrawing power of the substituents increases, whereas excited-state lifetimes decrease. The first oxidation step (0.74–0.86 V) and the reduction step are, respectively, assigned to π-electron removal or acceptance by the porphyrin ring. The second oxidation is assigned to removal of an electron from the ruthenium(II) center. The excited state is shown to be the $T(\pi{-}\pi^*)$ state of the porphyrin ring and to exhibit photoredox behavior involving both oxidative and reductive quenching. Redox product separation occurred in flash photolysis quenching experiments and back-reactions took place at near-diffusion-controlled rates. The redox potential of the Ru(TPP)(CO)$^{+/*}$ couple was estimated from emission and redox data to be −0.57 ± 0.03 V; it was determined from oxidative quenching studies to be −0.56 ± 0.10 V. Comparison to the excited-state properties of Ru(bpy)$_3^{2+}$ is made, and the utility of porphyrin complexes as potential solar energy storage catalysts is examined.

Introduction

Prior studies have shown that photoexcited states of metal-polypyridyl complexes can undergo oxidative[2] and reductive[3]

quenching. The ability of the excited states to undergo electron transfer has been utilized in a number of recent investigations for generating reactive redox intermediates. The excited states have provided the basis for energy related applications aimed at the eventual splitting of water photochemically. For example, hydrogen[4] and oxygen[5] have been produced separately in photoe-

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lectrochemical cells and by direct photolysis.[6,7]

Most of the research of this kind has been concerned with the excited state properties of ruthenium(II)–polypyridyl complexes. In particular, the lowest charge-transfer (CT) excited state of $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) has a lifetime of 0.8 μs,[8] reduction potentials for the $Ru(bpy)_3^{2+*/+}$ and $Ru(bpy)_3^{3+/2+*}$ couples are 0.82[3b] and –0.82 V, respectively,[9] and thermodynamically $Ru(bpy)_3^{2+*}$ is capable of reducing water to hydrogen and of oxidizing water to oxygen. Unfortunately, electron transfer to or from the excited state of $Ru(bpy)_3^{2+*}$ has found little direct use except for generating reactive intermediates whose practical applications are limited by their redox potentials or recombination reactions with $Ru(bpy)_3^+$ or $Ru(bpy)_3^{3+}$. It is obviously desirable to see if the redox chemistry found for $Ru(bpy)_3^{2+*}$ can be extended to new types of chemical systems both from the fundamental point of view and in terms of developing new photocatalytic systems which may have practical utility.

A few systems have been investigated as potential candidates. Some of these are polypyridyl complexes of other metals such as bis(2,9-dimethyl-1,10-phenanthroline)copper(I),[10] $Os(bpy)_3^{2+}$,[8] and $Fe(bpy)_3^{2+}$.[11] Organometallic compounds such as $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$[12] may have exploitable excited-state redox properties. Metal complexes of porphyrins are clearly of interest in this regard due to their role in photosynthesis and because of their high light absorptivity in the visible. Fong[13] and co-workers have reported the photochemical splitting of water by chlorophyll *a*. In addition, a photochemical scheme for oxidizing water has been proposed which suggests the use of a water-soluble manganese tetraphenylporphyrin complex as the photochemical catalyst.[14]

Excited states of metalloporphyrins are known to exhibit photoredox behavior involving both oxidative and reductive quenching.[15] Flash photolysis studies have given some insight into the possible nature of the photoactive excited state. For zinc uroporphyrin, Zn(UP), the excited state was shown to be the $T(\pi-\pi^*)$ state of the porphyrin ring.[15c] The triplet state was nonemitting at room temperature, had a lifetime of 2–8 ms depending upon the solution conditions, and underwent both oxidative and reductive quenching. Electron transfer from a short-lived, nonemitting excited state of $Ru(TPP)(py)_2$ (py = pyridine, TPP = tetraphenylporphyrin) in the presence of high concentrations of $Ru(NH_3)_6^{3+}$ has also been reported by Young et al.[15f]

In addition to strong light absorption in the visible, metalloporphyrins have other properties which make them appealing in potential photoredox applications.[16] (1) Excited-state lifetimes can be as long as milliseconds in some compounds, although they can be considerably shorter in others.[15c,f,17] (2) Electron-transfer quenching involves the $\pi-\pi^*$ level of the porphyrin ring[17] as opposed to the MLCT excited states in ruthenium(II)–polypridyl complexes. (3) Metalloporphyrins possess an extensive range and variety of redox behavior in their ground states.[18] (4) The ground-state redox behavior can be systematically changed by synthetically modifying the porphyrin ligand or changing the metal center.[18]

Our work reported here is an attempt to develop a new set of exploitable photoredox systems taking advantage of the innate properties of porphyrins cited above. We have focused our attention on defining the nature of the excited state for a series of para-substituted (tetraphenylporphine)ruthenium(II)–carbonyl complexes, Ru(p-XTPP)(CO), X = MeO, Me, H, F, Br, and Cl, and on investigating the role of the substituent X on excited-state lifetimes and redox potentials.

Experimental Section

Materials. The preparation and purification of the pyridinium salts used in the quenching studies were described previously.[19] Tetrabutylammonium hexafluorophosphate was obtained by preparative procedures previously published.[20] Metalloporphyrins Ru(p-MeOTPP)(CO)L, L = py and N-methylimidazole (N-MeIm), were prepared by the method of Eaton, Eaton, and Holm.[21] All other reagents were purchased commercially as reagent grade chemicals and used without further purification.

Preparation of Para-Substituted Tetraphenylporphyrins, H_2(p-XTPP), X = MeO, Me, H, F, Cl, Br. The procedure of Adler[22] was followed. Stoichiometric quantities of the appropriate para-substituted benzaldehyde and pyrrole were used. In a typical experiment, pyrrole (7.1 mL, 0.1 mol) and p-anisaldehyde (12.1 mL, 0.1 mol) were mixed in 750 mL of propionic acid, and the solution was heated at reflux for 30 min. The solution was allowed to cool slowly to room temperature during which time purple crystals precipitated. The crystals were collected by filtration, washed with methanol, and allowed to air-dry. The absorption spectrum of a CH_2Cl_2 solution of the product was consistent with formation of the resulting 5,10,15,20-tetrakis(p-methoxyphenyl)porphyrin.[23]

Preparation of Ru(p-XTPP)CO Complexes, X = MeO, Me, H, F, Cl, Br. Modifications of the procedures of Tsutsui[24] were used. In a typical experiment, 100 mg of $Ru_3(CO)_{12}$ and 100 mg of H_2TPP were added to a flask containing 30 mL of decalin. The mixture was heated under reflux for approximately 4 h and then allowed to cool to room temperature. The resulting solid was separated from the decalin solution by vacuum filtration. Methylene chloride was then added to the solid material, and the desired porphyrin was extracted along with other soluble impurities. The insoluble material was removed by filtration and discarded. The methylene chloride solution was then evaporated to dryness by using a rotary evaporator. The solid remaining in the flask was dissolved in benzene and added to a neutral alumina column developed in benzene. In some preparations the decalin solution contained appreciable amounts of the desired product, and it was also added to the alumina column above. Benzene was used to elute unreacted $Ru_3(CO)_{12}$, methylene chloride was used to elute unreacted H_2TPP, and a 50/50 methylene chloride/acetone solution was used to elute Ru(TPP)(CO). The green band characteristic of the chlorin impurity remained on the column. A visible spectrum of the methylene chloride/acetone fraction was obtained. Normally absorptions associated with H_2TPP were absent. However, an absorption at 600 nm characteristic of the chlorin impurity was sometimes present. In this case, the solution was evaporated to dryness, and the solid was rechromatographed until the 600-nm absorption was absent. The final solution was evaporated to dryness, and the resulting solid was dissolved in a small amount of tetrahydrofuran and

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Table I. Absorption and Emission Maxima and Emission Lifetime Data for Ru(*p*-XTPP)(CO) in $(CH_3)_2SO$

compd	absptn max,[a] nm	emissn max,[a,b] nm	$\tau_0{}^1$,[c,d] μs	$\tau_0{}^2$,[c,d] μs
Ru(*p*-MeOTPP)(CO)	569 (sh), 533, 417	733	32.1 ± 0.1	3.60 ± 0.04
Ru(*p*-MeTPP)(CO)	567 (sh), 532, 414	731	37.5 ± 0.1	2.12 ± 0.04
Ru(TPP)(CO)	565 (sh), 532, 413	729	36.0 ± 0.06[e]	1.79 ± 0.20[e]
			(36.3 ± 0.8)[f]	(1.86 ± 0.20)[f]
Ru(*p*-FTPP)(CO)	563 (sh), 532, 413	727	31.0 ± 0.1	1.08 ± 0.10
Ru(*p*-ClTPP)(CO)	564 (sh), 532, 414	726	25.3 ± 0.1	0.71 ± 0.10
Ru(*p*-BrTPP)(CO)	565 (sh), 532, 414	727	25.7 ± 0.1	0.78 ± 0.10

[a] ±1.0 nm. [b] Uncorrected. [c] Luminescence decay. A pulsed nitrogen laser was used for excitation (337.1 nm). Emission decays were followed at 738 nm. $\tau_0{}^2$ refers to luminescence decay of the decarbonylated photolysis product. Decays were exponential. [d] $T = 22.5 \pm 0.2 \,°C$. [e] $T = 22.8 \pm 0.2 \,°C$. [f] These values were determined by measuring the absorption decay of the triplet at 480 nm following laser excitation at 337 nm.

Table II. Half-Wave Potentials and Carbonyl Stretching Frequencies for Ru(*p*-XTPP)(CO) Complexes

compd	$E_{1/2}$,[a] V vs. SSCE			$\nu(CO)$,[d] cm^{-1}	4σ[e]
	Ru(*p*-XTPP)-(CO)$^{2+/+}$ [b]	Ru(*p*-XTPP)-(CO)$^{+/0}$ [b]	Ru(*p*-XTPP)-(CO)$^{0/-}$ [c]		
Ru(*p*-MeOTPP)(CO)	1.18	0.74	−1.35	1924	−1.072
Ru(*p*-MeTPP)(CO)	1.20	0.75	−1.35	1918	−0.680
Ru(TPP)(CO)	1.20	0.79	−1.32	1922	0.000
Ru(*p*-FTPP)(CO)	1.25	0.85	−1.28	1922	0.248
Ru(*p*-BrTPP)(CO)	1.25	0.86	−1.24	1923	0.928
Ru(*p*-ClTPP)(CO)	1.27	0.86	−1.24	1922	0.908

[a] ±0.01 V, μ = 0.2 M, 22 ± 2 °C; SSCE is the saturated sodium chloride calomel electrode. [b] In CH_2Cl_2. [c] In $(CH_3)_2SO$. [d] Determined in $(CH_3)_2SO$, ±1 cm^{-1}. [e] From J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, pp 162–177.

then was reprecipitated by the addition of hexanes. The absorption spectrum of the product was consistent with formation of Ru(TPP)-(CO).[25]

Emission and Quenching Measurements. Samples for quenching measurements in $(CH_3)_2SO$ contained Ru(TPP)(CO) ((1–3) × 10⁻⁵ M) and the appropriate concentration of quencher. In a typical experiment, six different concentrations of quenchers were placed in Pyrex tubes closed by rubber serum caps. The solutions were bubbled degassed with dry nitrogen for 30 min before emission measurements were made by using a Hitachi Perkin-Elmer MPF-A spectrofluorimeter.

Flash Photolysis Measurements. Samples for flash photolysis measurements were prepared in the same manner as for quenching measurements above. The freeze–thaw–pump–degas method was used to check whether small amounts of remaining oxygen affected lifetime or back-reaction rates. Both methods gave the same results. The conventional and laser flash photolysis spectrometers used have been described previously.[26]

Electrochemical Measurements. Cyclic voltammetric measurements were performed in $(CH_3)_2SO$ and CH_2Cl_2 solutions at a Pt button working electrode with 0.2 M [N(*n*-C₄H₉)₄](PF₆) as supporting electrolyte. The measurements were made vs. the saturated sodium chloride calomel electrode (SSCE). The cyclic voltammetric waves were reversible under the conditions of the experiment. The measurements were made with a PAR 174 polarographic analyzer in conjunction with a variable voltage range and sweep rate selector.

Visible–UV–IR Measurements. Visible–UV measurements were obtained with a Cary 14 and Bausch and Lomb/Shimadzu Spectronic 210. Infrared measurements were obtained by using a Perkin-Elmer 258 spectrophotometer. Solution spectra were obtained in matched cells for all the ruthenium porphyrins reported here.

Results

Absorption–Emission–Lifetimes. The results of absorption, emission, and lifetime experiments are given in Table I. Absorption maxima for Ru(TPP)(CO) are similar to those previously reported for that compound.[25] The emission maxima are shifted to longer wavelength from that observed for Ru(OEP)(CO),[27]

OEP = octaethylporphyrin. This shift is normal and consistent with changing the porphyrin ligand from the "natural" to the synthetic tetraphenyl derivative.[28]

Absorption and emission maxima for the other derivatives are shifted slightly from those of the parent compound. The shift is to lower energy as the electron donor ability of the substituent on the phenyl ring increases. The position of the emission wavelength maximum increases in the substituent order:

$$Br \simeq Cl \simeq F < H < Me < MeO$$
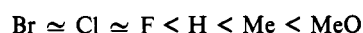
A single excited-state decay was observed by either transient absorption or emission measurements. The luminescence excited-state lifetime, $\tau_0{}^1$, also depends on the phenyl substituent in that it increases as the electron donor ability of the substituent increases. The sequence by substituent from longest to shortest lifetime is

$$Me > H > F > Br > Cl$$
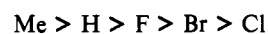
The notable exception is Ru(*p*-MeOTPP)(CO) which shows a decrease in lifetime rather than an increase.

During the lifetime measurements a second, more intense luminescence grows in as a function of photolysis time. The lifetime of the shorter-lived, second luminescence is labeled $\tau_0{}^2$ in Table I.

Ground-State Redox Potentials and Carbonyl Stretching Frequencies. The data obtained by cyclic voltammetric measurements for the half-wave potentials of Ru(*p*-XTPP)(CO) complexes are listed in Table II. The potentials were reversible on the oxidation side in CH_2Cl_2 and on the reduction side in $(CH_3)_2SO$. Reversibility was based on the ratio of anodic to cathodic peak currents (i_c/i_a) and on the potential separation of the peaks. The ratio of i_c/i_a was usually ~1.0, but the peak separation (~70 mV) was higher than the theoretical value of 59 mV. Higher values were also reported for Ru(OEP)(CO)(py) and justified on the basis of uncompensated solution resistance.[29]

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Table III. Stern–Volmer Constants and Rate Constants for the Quenching of Ru(TPP)(CO)* by Several Quenchers in (CH$_3$)$_2$SO

quencher	K_{sv},[a] M^{-1}	k_q,[b] M^{-1} s^{-1}	k_q',[c] M^{-1} s^{-1}
(1) [N-ethylphenazonium]$^+$ ion	9.02 × 10^4	2.50 × 10^9	1.49 × 10^{10}
(2) [N, N'-dimethyl-4,4'-bipyridinium]$^{2+}$ ion	2.39 × 10^4	6.64 × 10^8	7.75 × 10^8
(3) [N-methyl-4-cyanopyridinium]$^+$ ion	1.22 × 10^4	3.39 × 10^8	3.82 × 10^8
(4) [N-methyl-4-carbomethoxypyridinium]$^+$ ion	7.60	2.11 × 10^5	2.11 × 10^5
(5) N,N,N',N'-tetramethylbenzidine	6.73 × 10^2	2.02 × 10^7	2.03 × 10^7

[a] Determined using the equation $I_0/I = 1 + K_{sv}[Q]$. All intercepts were very close to 1, correlation coefficients were 0.99 ± 0.01, T = 23 ± 2 °C. [b] k_q was calculated from K_{sv} by using τ_0[Ru(TPP)(CO)*] = 36.0 μs (Table I, τ_0^1), ± 5%. [c] Calculated from $1/k_q = 1/k_q' + 1/k_D$ where k_D is the calculated diffusion rate constant, k_q is the rate constant for activated quenching, and k_q is the measured quenching rate constant.[32]
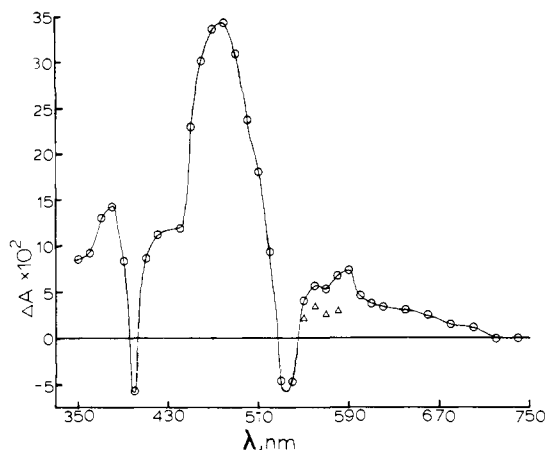
Figure 1. Difference spectrum at 50 μs following visible flash photolysis of a solution containing 4.2 × 10^{-6} M Ru(TPP)(CO) in (CH$_3$)$_2$SO. The triangles show the absorbance decrease following multiple flashes which occurs because of the slow decomposition of Ru(TPP)(CO).

The potentials are affected by the substituent bound to the phenyl ring. Reduction and oxidation potentials are shifted to more oxidizing potentials as the electron-withdrawing power of the substituent increases. The difficulty of oxidation increases along the substituent sequence

$$OMe < Me < H < F < Cl \simeq Br$$

The difficulty of reduction increases along the opposite sequence

$$Br \simeq Cl < F < H < Me \simeq MeO$$

The carbonyl stretching frequencies as listed in Table II remain fairly constant from compound to compound. This can be attributed to the fact that the substituent effect is primarily a σ effect and does not greatly perturb the π system of the metal–carbonyl bond.

Excited-State Properties of Ru(TPP)(CO). The excited-state properties of a series of related porphyrins were summarized in Table I. The emitting excited state of Ru(TPP)(CO) was investigated in more detail as a representative example of the class of compounds. A difference spectrum obtained 50 μs after conventional flash photolysis is shown in Figure 1. The spectrum, which gives the difference in absorptivity between the excited state of Ru(TPP)(CO)* and ground state of Ru(TPP)(CO), is in qualitative agreement with that obtained for Zn(UP)[15c] (also obtained by flash photolysis). As in the zinc complex, the excited state is presumably a porphyrin-based triplet excited state. As shown in Figure 1 by the data in the region 550–590 nm, a photodecomposition reaction occurs noticeably after multiple flashes. This is in accord with the observed photochemical behavior of Ru(TPP)(CO)(piperidine) in neat piperidine at 25 °C. For the complex, it was observed that irradiation in the visible region resulted in the relatively inefficient loss of CO (Φ = 10^{-4}–10^{-6}).[30] The decomposition was thought to occur by thermal activation from the emitting triplet level to higher ligand field states. Dolphin et al.[31] have taken advantage of the photosub-
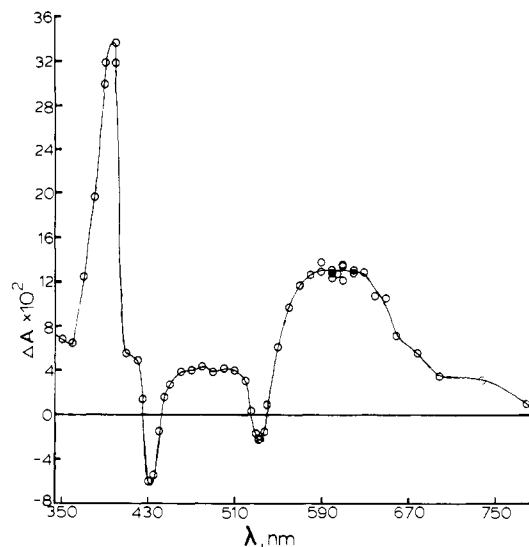

Figure 2. Difference spectrum at 50 μs following visible flash photolysis of a solution containing 1.6 × 10^{-3} M PQ^{2+} and 4.2 × 10^{-6} M Ru(TPP)(CO) in (CH$_3$)$_2$SO.

situion and have replaced CO by O$_2$ in Ru(OEP)(CO). Whitten et al.[27a] have utilized this property to prepare disolvated ruthenium–porphyrin complexes of the type Ru(OEP)S$_2$ photochemically. Thus, it is reasonable to propose that the decomposition product observed here is probably Ru(TPP)((CH$_3$)$_2$SO)$_2$ and that the disolvento complex is the origin of the short-lived luminescence (note τ_0 values in Table I) that grows in during the flash photolysis experiments.

Redox Properties of Ru(TPP)(CO)*. Stern–Volmer constants, observed quenching rate constants, and quenching rate constants corrected for diffusional effects are listed in Table III. In most cases the quenching reactions were rapid but slower than the diffusion-controlled limit.[32] The observed quenching rate constant for paraquat[33,34] (MeNC$_5$H$_4$–C$_5$H$_4$NMe^{2+}, PQ^{2+}) was 6.6 × 10^8 M^{-1} s^{-1}; the calculated diffusion-controlled rate constant was 4.6 × 10^9 M^{-1} s^{-1}. The observed rate constant for quenching by

(30) Vogler, E. M.; Kunkely, H. *Ber. Bunseges. Phys. Chem.* **1976**, *80*, 425.

(31) Farrell, N.; Dolphin, D. H.; James, B. R. *J. Am. Chem. Soc.* **1978**, *100*, 324.

(32) For the diffusion calculations described here and those described later, an average van der Waals radius of 8.2 Å was used for Ru(TPP)(CO)$^+$, Ru(TPP)(CO), and Ru(TPP)(CO)* and an average van der Waals radius of 3.8 Å was used for the various quenchers. The average values were estimated by taking the average of the van der Waals dimensions along the three molecular axes. k_D for quenching was calculated by using the Smoluchowski equation[33] $k_D = 2RT/3000\eta(2 + r_A/r_B + r_B/r_A)$, where the Stokes–Einstein equation has been used to calculate diffusion coefficients for the reactants of radii r_A and r_B in a medium of viscosity η. The Debye–Smoluchowski equation[34] $k_D = 2RT/3000\eta(2 + r_A/r_B + r_B/r_A)f$ was used to calculate k_D for the back-reaction of PQ$^+$ with Ru(TPP)(CO)$^+$. f is the integral $[a\int_a^\infty (e^u/kT) \, dr/r^2]^{-1}$ and $u = (Z_A Z_B e^2/D_s)[e^{\kappa a}/(1 + \kappa a)]e^{-\kappa r}/r$, where the various terms are r = distance of separations of the ions, a = distance of closest approach of the ions = $r_A + r_B$, D_s = static dielectric constant of (CH$_3$)$_2$SO, Z_A and Z_B = charges of ions, e = electrostatic charge, $\kappa = (8N_0 e^2 \mu/1000 D_s kT)^{1/2}$; N_0 = Avogadro's number, and μ = ionic strength. The integral was evaluated using Simpson's rule.

(33) Smoluchowski, M. Z. *Phys. Chem.* **1917**, *92*, 129.

(34) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

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N,N,N',N'-tetramethylbenzidine $(Me_2NC_6H_5-C_6H_5NMe_2$, TMBZ) was 2.0×10^7 M^{-1} s^{-1}.

The nature of the quenching process was determined by flash photolysis studies. Paraquat, PQ^{2+}, which is known to quench excited states oxidatively,[35] was chosen as a representative example of the first four types of quenchers in Table III. The difference spectrum obtained following flash photolysis of $(CH_3)_2SO$ solutions containing $Ru(TPP)(CO)$ and PQ^{2+} is shown in Figure 2. Qualitatively, the spectrum is exactly what is expected for a composite of $Ru(TPP)(CO)$ bleaching, $Ru(TPP)(CO)^+$ absorbance, and PQ^+ absorbance (PQ^{2+} is transparent in the visible region of the spectrum) based on available spectra in organic solvents.[36,37] The back-reaction (eq 1) between PQ^+ and Ru-

$$PQ^+ + Ru(TPP)(CO)^+ \rightarrow PQ^{2+} + Ru(TPP)(CO) \quad (1)$$

$(TPP)CO^+$ was followed at 605 nm, and the rate constant was determined to be $(1.72 \pm 0.02) \times 10^9$ M^{-1} s^{-1}, which is similar to the calculated diffusion-controlled rate constant of 2.3×10^9 M^{-1} s^{-1}.[32] In contrast to the photodecomposition problems observed in Figure 1, no decrease or change in the difference spectrum upon repeated flashing was observed in solutions which contained PQ^{2+}.

Reductive quenching was also examined by flash photolysis studies in $(CH_3)_2SO$ solutions. When solutions containing Ru-(TPP)(CO) and the known reductive quencher[38] TMBZ were flashed, a rapid quenching of the excited state occurred

$$Ru(TPP)(CO)^* + TMBZ \rightarrow Ru(TPP)(CO)^- + TMBZ^+ \quad (2)$$
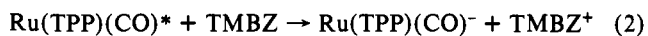
as shown by the spectral appearance of the ions despite the Coulombic attraction between them. The back-reaction

$$Ru(TPP)(CO)^- + TMBZ^+ \rightarrow Ru(TPP)(CO) + TMBZ \quad (3)$$
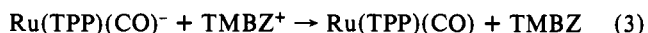
was followed, and the rate constant was estimated to be $(6 \pm 3) \times 10^9$ M^{-1} s^{-1}.[39] In another experiment, flash photolysis of solutions containing $Ru(TPP)(CO)$ and sodium dithiocarbamate, DTC^-, resulted in the irreversible production of a dark product in solution, presumably $Ru(TPP)(CO)^-$. DTC· is known to dimerize extremely rapidly in solution upon its production in flash photolysis experiments.[40]

Discussion

Electronic Structure of Ru(p-XTPP)(CO). Several recent papers have been devoted to the electrochemistry of synthetic, substituted porphyrins and metalloporphyrins.[41] In nonaqueous media, porphyrins and metalloporphyrins can be oxidized[42] in single-electron transfer steps to yield the cation and dication or reduced[43] in two single-electron transfer steps to yield the anion and dianion. In the study reported here, Ru(p-XTPP)(CO) was observed to undergo the first two oxidation steps, but only the first reduction step was reversible in $(CH_3)_2SO$.

For the first oxidation step (the Ru(p-XTPP)(CO)$^{+/0}$ couples in Table II), it is reasonable to assume that an electron is lost from a π level of the porphyrin ring. The assumption is reasonable given Brown's[29] assignment for the first oxidation in Ru(OEP)(CO)(py). The dependence of $E_{1/2}$ on Hammett σ_p values (vs. 4σ here for the 4 substituents/porphyrin) is illustrated in Figure 3. The

(35) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710.

(36) Brown, G. M.; Hopf, F. R.; Ferguson, J. A.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5939.

(37) Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524.

(38) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

(39) k_b is assumed to be equal to k_D. The spectrum of Ru(TPP)(CO)$^-$ was unavailable. There is reasonable agreement between $\Delta\epsilon$ values calculated by using $k_D = k_b$ and those one would expect for a reduced porphyrin.[15c]

(40) Deronzier, A.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 2912.

(41) (a) Giraudeau, A.; Callot, H. J.; Gross, M. *Inorg. Chem.* **1979**, *18*, 201. (b) Giraudeau, A.; Callot, H. J.; Jordon, J.; Ezhar, I.; Gross, M. *J. Am. Chem. Soc.* **1979**, *101*, 3857. (c) Walker, F. A.; Beroiz, D.; Kadish, K. M. *Ibid.* **1976**, *98*, 3484.

(42) Manassen, J.; Wolberg, A. *J. Am. Chem. Soc.* **1970**, *92*, 2982. Felton, R. H.; Fajer, J.; Borg, D. C.; Dolphin, D. *Ibid.* **1970**, *92*, 3451. Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* **1974**, *7*, 26.

(43) Clark, D. W.; Hush, N. S. *J. Am. Chem. Soc.* **1965**, *87*, 4238. Felton, R. H.; Linschitz, H. *Ibid.* **1966**, *88*, 1113.
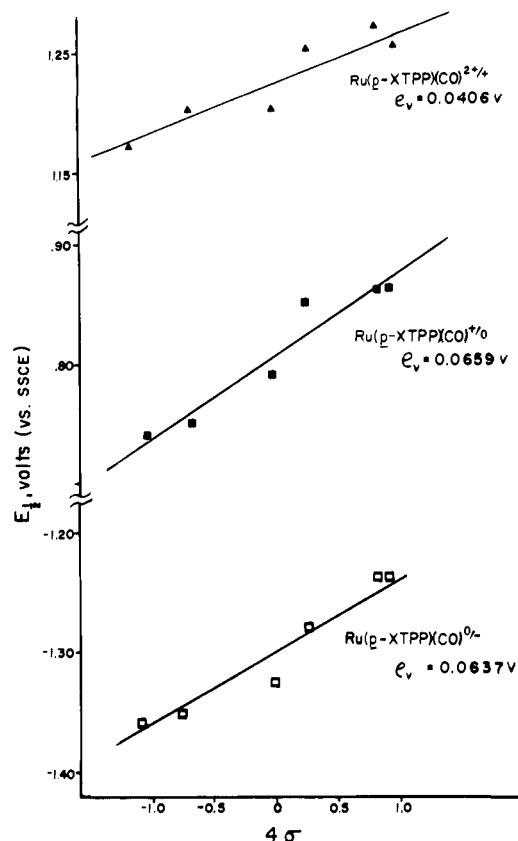

Figure 3. Hammett plot: comparison of the $E_{1/2}$ values of para-substituted (tetraphenylporphyrin)ruthenium–carbonyl complexes vs. the Hammett substituent constant. Data are taken from Table II.

dependence is linear and has a slope, ρ_v, of 0.065 V. This is in the range of 0.085 V Walker[41c] found for a similar series of cobalt porphyrin oxidations in CH_2Cl_2 where the ring was assigned as the position of oxidation. In addition, Gouterman's[27b] iterative extended Hückel (IEH) calculations indicate that the highest occupied molecular orbital for Ru(OEP)(CO)(py) is an $a_{2u}(\pi)$ orbital on the porphyrin ring.

The phenyl ring substituents have a similar effect on the potentials for the reduction step. The value of ρ_v is 0.062 V (Figure 3). Gross[41a] found that β substituents had about twice the effect on the electrochemical reduction of the π system than it had on oxidation of the pyrrolic nitrogen lone pair. Similarly, the substituent effect on $E_{1/2}$ for oxidation or reduction of the metal in metalloporphyrins was always found to be smaller than that of the ring.[41b] Walker[41c] reported that ρ_v for oxidation or reduction of the cobalt center in para-substituted tetraphenylporphyrins was about $1/2$ that of the ring π system. In addition, the IEH calculations of Gouterman[27b] lead to the assignment that the $e_g^*(\pi)$ level located on the porphyrin ligand is the lowest unoccupied molecular orbital. The accumulated evidence indicates that reduction occurs in the π system of Ru(p-XTPP)(CO) complexes.

The difference between the potentials for the couples involved in the first oxidation and reduction steps, $\Delta E = E_{1/2}^{ox} - E_{1/2}^{red}$, is often taken to estimate the first $\pi-\pi^*$ transition in the visible region of the spectrum.[44] Before this equation can be applied to the system studied here, two corrections must be applied. The data in Table II were collected in two different solvents. The oxidations were reversible in CH_2Cl_2 but could not be studied in $(CH_3)_2SO$. The first reduction was reversible in $(CH_3)_2SO$, but not in CH_2Cl_2. The first correction factor is based on the reversible reduction of Ru(p-MeOTPP)(CO)(py) in both solvents. Reversible reductions were found at -1.65 ± 0.01 V (vs. SSCE) and at -1.37 ± 0.01 V (vs. SSCE) in CH_2Cl_2 and $(CH_3)_2SO$, respectively. In order to reference all measurements to $(CH_3)_2SO$,

(44) Fuhrhop, J. H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140.

we added 0.28 V to the potentials for the oxidative couples measured in CH_2Cl_2.

The second correction makes an energy adjustment for the effect of solvent on the molecular orbitals of the compound. A value of −0.25 V has been derived for this contribution.[18a] Combining the two correction factors leads to a calculated ΔE value for Ru(TPP)(CO) of 2.14 V. This is in close agreement to the experimental value of 2.19 V.

The second oxidation may come from either the metal or porphyrin (eq 4 and 5).

$$Ru^{II}(P^+)(CO) \xrightarrow{-e^-} Ru^{III}(P^+)(CO) \qquad (4)$$

$$Ru^{II}(P^+)(CO) \xrightarrow{-e^-} Ru^{II}(P^{2+})(CO) \qquad (5)$$
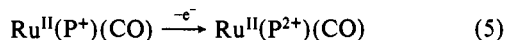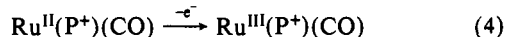
The difference in potential between the first and second oxidation steps in Table I is 0.42 ± 0.02 V. The potential difference is beyond the range of 0.29 ± 0.05 V found for a series of metalloporphyrins and porphyrins where both oxidations are known to be porphyrin based.[44] The ρ_v value of 0.040 V (Figure 3) is also less than the 0.065-V value associated with oxidation at the ring π system but may be consistent with oxidation of Ru^{II} to Ru^{III} (eq 4).

When potentials for the Ru(p-XTPP)(CO)$^{2+/+}$ couples in Table I are analyzed by first making the 0.28-V correction for the difference in solvents cited earlier, they fall in the region of $Ru^{III/II}$ couples for polypyridyl complexes like Ru(bpy)$_3^{3+/2+}$. The inferred Ru(III)/Ru(II) potentials are considerably more positive than the potential for the Ru(TPP)(py)$_2^{+/0}$ couple (0.42 V vs. SSCE in HCON(CH$_3$)$_2$),[15f] showing that the d electrons of the ruthenium center in porphyrins studied here are considerably stabilized by π-bonding interactions and the net effect is much the same as in polypyridyl complexes. The origin of the back-bonding effect probably lies largely with the CO group,[36] but the couple involves oxidation of Ru(II) bound to ring oxidized porphyrin, [Ru^{II}-(TPP)(CO)]$^+$ ⇌ [Ru^{III}(TPP)(CO)]$^{2+}$, and the oxidized porphyrin may also have enhanced π-back-bonding capabilities compared to unoxidized porphyrin. It is interesting to note in this respect that the Ru–N bond distance in Ru(bpy)$_3^{2+}$ [45] and the Ru–N(porphyrin) in Ru(TPP)(CO)(py)[46] are 2.056 and 2.052 Å, respectively. The short bond distance in Ru(bpy)$_3^{2+}$ was interpreted as resulting from extensive π back-bonding between the metal t$_{2g}$ orbitals and the π^* orbitals of the bipyridine ligands, but it is not clear that dπ(Ru) → π^*(porphyrin) back-bonding is significant in the metalloporphyrins. The importance of dπ(Ru) → π^*(CO) back-bonding can be seen in the ν(CO) stretching frequency. The stretch is at 1922 cm^{-1} compared to 2143 cm^{-1} for uncomplexed CO.[47]

Luminescence in metalloporphyrins is generally associated with the π,π^* system of the porphyrin ring. In a number of compounds both shorter lived fluorescence and longer lived phosphorescence are found.[17] Only one prominent emission near 730 ± 10 nm was observed for Ru(p-XTPP)(CO) compounds. From the lifetimes observed (Table I) it is reasonable to assign the emission as coming from a T(π,π^*) excited state. A similar assignment has been made for emission from Ru(TPP)(CO)(piperidine)[30] and Ru(OEP)-(CO)(py).[27] In addition, the difference spectrum of Ru(TPP)(CO) and Ru(TPP)(CO)* in Figure 1 is similar to that of the Zn(UP) system,[15c] particularly where the characteristic absorptions of the triplet state in the 450–600-nm region of the spectrum are observed.

Luminescence lifetimes for Ru(p-XTPP)(CO) complexes were 30 ± 10 μs at 25 °C. This is shorter than the lifetime of 405 μs reported for Ru(OEP)(CO)(py) at 77 K[27b] which is not unexpected given the difference in temperature between these two experiments. The excited state lifetimes also depend on substituent effects
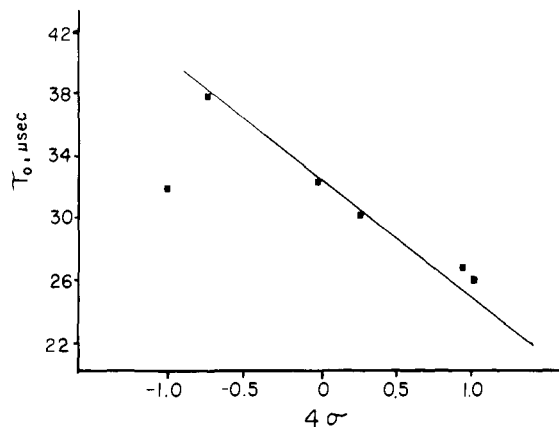
(45) Rillema, D. P.; Jones, D. S.; Levy, H. *J. Chem. Soc., Chem. Commun.* **1979**, 849.
(46) Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 8583.
(47) Cotton, F. A.; Wilkinson, F. R. S. In "Advanced Inorganic Chemistry", 3rd ed.; Interscience; New York, 1972; Chapter 22.

Figure 4. Plot of the phosphorescence lifetimes (μs) for the T(π,π^*) porphyrin state vs. the Hammett σ parameter. Data are taken from Tables I and II.

(Figure 4). In Figure 4 the slope of the linear portion of the plot of τ_0^1 vs. σ is −7.6 ± 0.1 μs and the correlation coefficient is 0.998. The notable exception to the linear relation is Ru(p-MeOTPP)(CO) which has a shorter lifetime than the general trend would predict.

The negative slope of the plot in Figure 4 is opposite to that for the dependence of the half-wave potentials on σ_p. Thus, lifetimes become shorter as the electron withdrawal ability of the substituent increases. There is no apparent correlation of the lifetime data with what has previously been referred to as the internal heavy-atom effect, where excited-state lifetimes of Zn-(p-XTPP), X = H, Cl, Br, and I, were reported to decrease as the mass of the halogen increased.[48] Additional work with more systems is needed to clarify this difference in behavior between the two systems.

Redox Properties of the Excited State. Redox properties of the Ru(TPP)(CO) excited state were similar to those of Ru-(bpy)$_3^{2+}$* in that with either reductive or oxidative quenchers, electron-transfer reactions occur to or from the excited state, redox product separation occurs, and electron back-transfer reactions can be followed by flash photolysis. For Ru(bpy)$_3^{2+}$ it has been possible to study thermal redox reactions with near-diffusion-controlled rates induced by excited-state quenching, and it is clear that similar experiments can be carried out on the basis of electron-transfer quenching of Ru(TPP)(CO).*

Of particular concern is the energy of the emitting $\pi-\pi^*$ state above the ground state and the redox potentials of the excited state. A lower limit for the excited-state internal energy content above the ground state was calculated from the emission maxima as 1.70 ± 0.01 eV for the series of compounds. The value is a lower limit since it includes a contribution from vibrational distortions between ground and excited states and is not the true energy difference between the two thermally equilibrated states. However, with use of the estimated excited state energies, reduction potentials for Ru(p-XTPP)(CO)$^{0/-}$ and Ru(p-XTPP)(CO)$^{+/0}$ couples, and $T\Delta S \approx 0.03$ V because of the difference in spin multiplicity between excited and ground states, estimates can be made for the Ru(p-XTPP)(CO)$^{+/*}$ and Ru(p-XTPP)(CO)$^{*/-}$ couples. The potentials are −0.57 ± 0.03 V and 0.37 ± 0.04 V, respectively.

The validity of the spectroscopic procedure can be tested by determining the excited-state redox potential of Ru(TPP)(CO) by electron-transfer quenching.[9] A series of four oxidative quenchers were chosen which varied in reduction potentials from −0.09 to −0.78 V. Figure 5 illustrates the dependence of $RT \ln k_q'$ on the reduction potential of the quenchers. The dependence is expected to be linear at low $E_{1/2}[Q/Q^-]$ (slope = $^1/_2$ or 1 V) and approach a limiting value at higher $E_{1/2}[Q/Q^-]$. The plot in Figure 5 indicates that such is the case qualitatively, but there

(48) Solovev, K. N.; Tsvirko, M. P.; Gradyushko, A. T.; Kozhich, D. T. *Opt. Spectros.* **1972**, *33*, 480.

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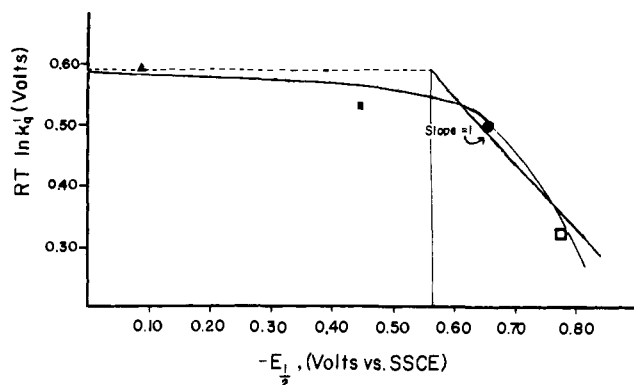
Figure 5. Plot of $RT \ln k_q'$ (V) vs. $E_{1/2}$ (Ox/Red) in $(CH_3)_2SO$ at 22 ± 2 °C for the quenching of Ru(TPP)(CO) by (▲) N-ethylphenazonium ion, (■) N,N'-dimethyl-4,4'-bipyridinium ion (paraquat), (●) N-methyl-4-cyanopyridinium ion, and (□) N-methyl-4-carbomethoxy-pyridinium ion. Data are taken from Tables II and III. The experimental slope is 1.6. A line of slope 1 is shown drawn midway between the two points which was used for estimating $E_{1/2}$ for the Ru(TPP)-(CO)$^{+/*}$ couple.

Scheme I
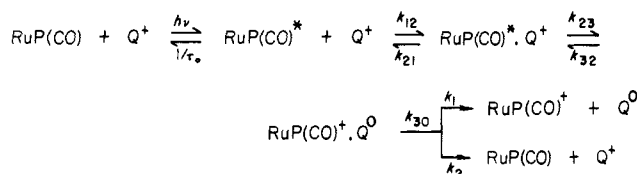
are not sufficient points to define the shape of the curve in detail.

The limiting case of unit slope has been derived on the basis of the kinetic scheme of Rehm and Weller[49] for fluorescence quenching of a series of aromatic excited states. In the context of the system dealt with here, the kinetic scheme becomes Scheme I. The resultant equation derived[38] for oxidative quenching where $k_{32} \gg k_{30}$ is

$$RT \ln k_q' = RT \ln k_{30}K_{12} + E(Q/Q^-) - [E(Ru(TPP)(CO)^{+/*}) + W_p - W_r] \quad (6)$$

Equation 6 contains work terms associated with Coulombic interactions of reactants (W_r) and products (W_p) which are relatively small ($W_r = 0$ for each case here except for PQ^{2+} as quencher). When $E(Q/Q') = E(RuTPP(CO)^{+/*})$, it follows that $RT \ln k_q' = RT \ln k_{30}K_{12}$. If it is assumed that $RT \ln k_{30}K_{12}$ is 0.59 V[50] then at the value of $RT \ln k_q' = 0.59$ V, it follows that $E_{1/2}[Q/Q^-] \approx -E(RuTPP(CO)^{+/*})$, giving a value of -0.56 ± 0.10 V for the Ru(TPP)(CO)$^{+/*}$ couple. This value is in good agreement with the spectroscopically derived value.

A comparison between ground- and excited-state redox potentials of Ru(TPP)(CO) and Ru(bpy)$_3^{2+}$ is made in Figure 6. The excited state potentials for the Ru(TPP)(CO)$^{+/*}$ and Ru-(TPP)(CO)$^{*/-}$ couples fall between those of the Ru(bpy)$_3^{2+*}$ couples, showing that the π,π^* excited state for Ru(TPP)(CO)* is thermodynamically less powerful as both oxidant and reductant compared to Ru(bpy)$_3^{2+*}$. Potentials for the excited state couples are shifted somewhat for the other ruthenium porphyrins and depend upon the substituent. The shifts, however, are not dramatic for this series of compounds.

An examination of the excited state behavior of $(CH_3)_2SO$ solutions containing Ru(p-MeOTPP)(CO)(py) revealed mostly

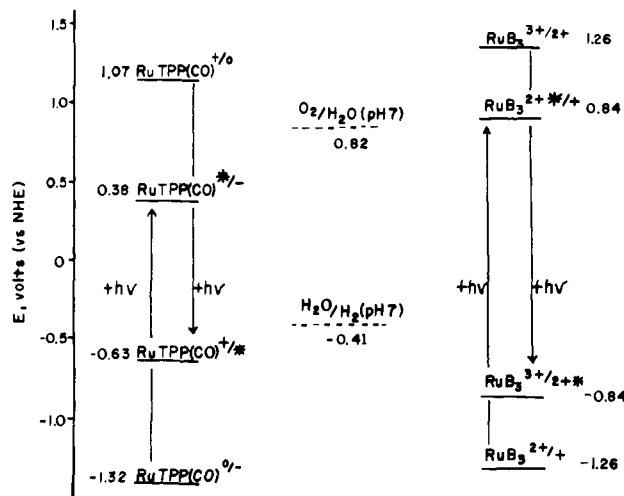**Figure 6.** Redox potential diagram comparing Ru(TPP)(CO) to RuB_3^{2+} and H_2O. B = bipyridine.

similarities to that of the solvated species,[53] with minor shifts consistent with an increase in electron density of the porphyrin complex. The emission maximum moved from 733 to 738 nm and the emission lifetime τ_0^1 increased from 32.1 to 34.9 μs. The reduction potential (−1.36 V) shifted by only 0.01 V in $(CH_3)_2SO$. Comparison to the reduction potential of Ru(p-MeOTPP)-(CO)(N-MeIM) in CH_2Cl_2 (−1.38 V) revealed a shift of only 0.02 V. In a more normal case exemplified by $Co^{III/II}(p\text{-MeOTPP})L_2$, the difference between the reduction potential for L = py and N-MeIM was 0.24 V.[54] The inability to significantly alter excited-state and redox potentials by changing L in the coordination sphere of Ru(p-XTPP)(CO)L suggests weak bonding along that direction. This is consistent with the long Ru–N(pyridine) bond distance[46] of 2.186 Å in Ru(TPP)(CO)(py) and the known lability of L in that coordination site.[21]

Conclusions

The excited-state properties of Ru(TPP)(CO)* appear to be well-defined, and its redox properties are exploitable in schemes similar to those developed for Ru(bpy)$_3^{2+*}$. Both of the excited states have water-reducing capability, although for Ru(TPP)-(CO)* it is marginal (Figure 6). In addition, redox potentials of reactive intermediates are approximately the same. These facts and the fact that reversible electron-transfer reactions of Ru(TPP)(CO) took place with little decomposition in the presence of a quencher suggest that porphyrins should be explored as potential photochemical energy storage catalysts.

Some important features which make metalloporphyrins so desirable in this respect are their strong visible light absorption capability and the ability to alter redox and excited-state properties by varying ring substituents and metal centers. The effect was small for Ru(p-XTPP)(CO) systems, but it is reported to be much more significant for other porphyrin ring substituents.[41a,b,55] This means that as long as the excited state is π–π^*, that changes in the nature of the ligand and/or the metal will lead to controllable excited-state properties—thermodynamically.

(49) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834.

(50) $RT \ln k_{30}K_{12}$ was estimated in the following way: K_{12} was calculated from the Fuoss–Eigen equation[51,52] $K = (2.524 \times 10^{-3})d^3 \exp-(W_r/RT)$. K_{12} = 4.4 for the quenching reactions ($W_r = 0$, $d = 12.03$ Å). $k_{30} = k_1 + k_2$ and $k_1 \approx k_2$ since redox products were observed during flash photolysis. k_1 can be estimated from $K = k_1/k_{-1}$ for the equilibrium $RuTPP(CO)^+,PQ^+$ (k_1) ⇌ $RuTPP(CO)^+ + PQ^+$ (k_{-1}). From the Fuoss equation, $K = 0.84$ ((CH_3)$_2$SO), $k_{-1} = k_D = 1.72 \times 10^9$ M^{-1} s^{-1},[32] $D_s = 48.9$, $Z_A = +1$, $Z_B = +1$, $\mu \simeq 0$). $k_1 = 1.4 \times 10^9$ M^{-1} s^{-1}. $RT \ln k_{30}K_{12} \simeq 0.59$ V.

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(52) Hemmes, P. *J. Am. Chem. Soc.* **1972**, *94*, 75.

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