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Photochemical Redox Reactivity of Dimeric and Monomeric Copper(II) and Cobalt(II) Sulfophthalocyanines

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Received February 23, 1978

The dimeric copper(II) and cobalt(II) sulfophthalocyanines are dissociated into oxidized and reduced metastable species by ultraviolet photolyses. The intermediates, studied by flash photolysis, were characterized as copper(II)–ligand radical species and sulfophthalocyanines containing Co(I) and Co(III) metal centers. Stable products were not formed in the absence of appropriate scavengers. Photochemical redox tendencies were observed also in photolyses of monomeric species in the presence of alcohols. Quantum yields demonstrate that this reactivity arises from the population of an upper excited state. The possible nature of such a state is discussed.

Introduction

The properties of the phthalocyanines have received a great deal of attention. Oxidation and reduction processes of such species have been the subject of a number of studies.[1-7] They have proved that the oxidation state of either ligand or metal center can be modified by one-electron redox reactions. Also, efforts have been devoted to the spectroscopic properties of the low-lying excited states of these compounds.[8] It is clear that the major contribution to the absorption spectra of phthalocyanine complexes arises in π–π^* transitions.[9,10] However, the excited states, populated in these transitions, have been labeled using an ordering of molecular orbitals which has been subject to criticisms.[10] Moreover, there is little information concerning the photochemical transformations of these compounds in fluid solutions.[11] Some studies have been recently carried out using porphyrins.[12,13] The mediation of these compounds in the photochemical oxidation of the solvent has been demonstrated. Such behavior has been related to the formation of complexes between an $n\pi^*$ excited state of the dye and some hydrogen-donor species.

The photochemical behavior of the copper(II) and cobalt(II) sulfophthalocyanines in aqueous solutions was studied in this work.[14] The dissociation of the dimeric species $[M(PTS)]_2^{8-}$, M = Co(II) and Cu(II), by means of redox processes, was induced by irradiation in ultraviolet bands. Moreover, redox photochemical reactions were also observed with monomeric species $[M(PTS)]^{4-}$, M = Co(II) and Cu(II).

Experimental Section

Photochemical Procedures. A Rayonet merry-go-round reactor with low-pressure mercury lamps ($I_0 = (8.3 \pm 0.4) \times 10^{-4}$ einstein/(L min)) was used for irradiations at 254 nm. Continuous photolyses were also carried out at various wavelengths (225–550 nm). The experimental arrangement, used in such experiments, consists of a 300-W Eimac Varian lamp combined with a Bausch and Lomb monochromator, collimating lenses, and filters. Ferrioxalate[15] and Reinecke[16] salts were used as primary actinometric references. The light intensity for irradiations at 225–300 nm was frequently tested with $Co(NH_3)_5Br^{2+}$.[17]

Quantum yields were obtained using the following procedure. Solutions, used in such determinations, absorbed more than 99.99% of the incident light (optical density ≥4 at the excitation wavelength). Product concentrations were obtained at various periods of the irradiation. The slopes of the curves of the product concentration vs. time, extrapolated to zero time, were used for yield calculations.

Solutions were deaerated with solvent-saturated nitrogen streams. The relative amount of dimeric to monomeric species in these solutions was determined by means of the absorption spectra. This ratio was investigated for each of the experimental conditions used throughout this work. Photolyses were also carried out in presence of oxygen using solutions equilibrated under 1 atm of O_2.

The flash photolysis apparatus was described elsewhere.[18] Nevertheless, some of the basic features will be indicated here. Two FP-8-100 C Xenon Corp. flash lamps were fired in series at energies adjusted to values between 250 and 40 J/pulse. A lifetime of 30 μs was measured for the flash pulse under these conditions. Hence, points for either kinetics or spectra determinations were regarded significant only for times equal to or longer than 50 μs. The spectra reported at zero time were obtained by extrapolating back to zero time from appropriate first- or second-order graphics. Solutions were protected from the ultraviolet and infrared light of the monitor beam with various filters and 10 cm of distilled water. The deaeration of these solutions was carried out with nitrogen, and liquids were transferred to the reaction cell in a gastight apparatus.

Analytical Procedures. Analyses for irradiation products and free aqueous metal ions $Cu(aq)^{2+}$ and $Co(aq)^{2+}$ were made by ion-exchange chromatography. The anion exchanger resin, 5–10 cm^3 of Amberlite IR-45, was activated with 100 cm^3 of 2 M HCl and washed with 100 cm^3 of distilled water. Sample ($\sim$3 cm^3) solutions were passed through the activated resin, and the parent sulfophthalocyanine complexes were retained in the column. Cationic and neutral species were eluted with 0.1 M NaCl and collected in 3-cm^3 samples. Tests carried out with solutions containing mixtures of the metal phthalocyanines and the corresponding metal ion revealed that they can be neatly separated by this procedure.

The concentration of reduced $[Cu(P\dot{T}S)]^{5-}$ was measured by two different procedures. The formation of this species was followed and measured by the absorbance increments observed at 550 nm. Moreover, these results were compared with those obtained when such species were titrated with 10^{-4} M Fe^{3+}. The concentration of $[Co^{III}(PTS)]^{3-}$ was estimated from the absorption spectra of irradiated solutions. Positive and negative increments of the absorbance were measured at 320, 620, and 660 nm. Calibration curves were obtained using mixtures of cobalt(II) and cobalt(III) sulfophthalocyanine.

Formaldehyde was determined by means of the chromotropic acid procedure in irradiated solutions.[19] Blanks were prepared with solutions kept in the dark.

Materials. Sodium (sulfophthalocyanine)cuprate(II) was purchased from Eastman and purified according to ref 20. Sodium (sulfophthalocyanine)cobaltate(II)[20] and sodium hydroxo(sulfophthalocyanine)cobaltate(III)[21] were obtained and purified using procedures reported by Weber and Busch. Other materials used in this work were reagent grade and they were used without further purifications.

Results

1. Flash Photolysis. Copper(II) Sulfophthalocyanine. Flash photolysis of the sodium salt of dimeric (phthalocyaninetetrasulfonato)cuprate(II), $[Cu(PTS)]_2^{8-}$,[14] was carried out in deaerated acidic solutions (10^{-1} M $\geq [HClO_4] \geq 10^{-5}$ M). A transient spectrum with maxima at 535 and 570 nm, Figure 1a, was in agreement with a process where Cu(II) ligand radicals $Cu(P\dot{T}S)^{5-}$[1] and $Cu(P\dot{T}S)^{3-}$[7] were produced during the life of the flash. These absorptions disappear by a reaction with a second-order dependence on transient concentration (Figure 2a).[22] A ratio of the rate constant to the extinction coefficient, $k/\epsilon = (5.7 \pm 0.3) \times 10^4$ cm s^{-1}, was obtained when such a reaction was followed at 520 nm. No permanent changes of the solution spectrum were detected under these conditions (see also continuous photolysis). Moreover, repeated flash irradiation of the same solution (10 pulses—250 J/flash) did not produce a noticeable change of the solution spectrum.

Alcohols, 2-propanol, methanol, and *tert*-butyl alcohol, were used as scavengers of the intermediates. The decay of the

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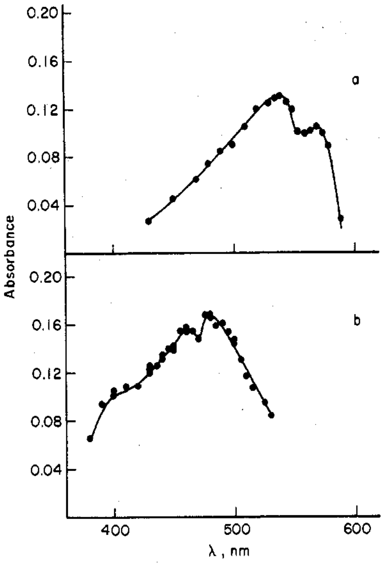

Figure 1. Spectra of species generated in flash irradiations. Absorptions developed 50 μs after the flash in (a) deaerated acidic (10^{-1} M $HClO_4$) solutions of $[Cu(PTS)]_2^{8-}$ and (b) deaerated acidic (10^{-1} M $HClO_4$) solutions of $[Co(PTS)]_2^{8-}$. The flash energy was 250 J/pulse.

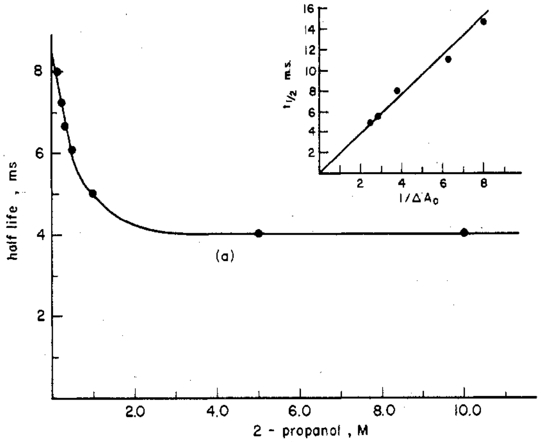

Figure 4. Half-lifetime, $t_{1/2}$, of the absorptions produced in flash photolyses of acidic (10^{-1} M $HClO_4$) $[Cu(PTS)]_2^{8-}$ solutions. Dependence on 2-propanol concentration when irradiated with pulses of 250 J/flash (a) and on the reciprocal of the initial transient absorption, ΔA_0, measured at 510 nm when [2-propanol] = 3 M and 40 ≤ energy/flash ≤ 250 J.

absorption was gradually inhibited by increasing concentrations of 2-propanol ($[(CH_3)_2CHOH] \leq 10$ M), Figures 3[22] and 4. The spectrum of the stable product obtained in photolyses of deaerated solutions of $[Cu(PTS)]_2^{8-}$ in 10^{-1} M $HClO_4$ and 1.0 M 2-propanol shows absorbance changes that can be explained if this species is the reduced copper(II)–ligand radical $[Cu(P\dot{T}S)]^{5-}$, reported by Rollman and Iwamoto (see ref 1 and "Continuous Photolysis" section).

The disappearance of the transient, generated in flash irradiations of deaerated solutions of $[Cu(PTS)]_2^{8-}$ in 0.1 M $HClO_4$, was studied as a function of the alcohol concentration (0.1 M ≤ $[(CH_3)_2CHOH]$ ≤ 10 M). This reaction shows a complex behavior under these experimental conditions which is discussed next. The half-life of the absorbance decay decreases rapidly with increasing 2-propanol concentration, and a limit is reached for ~1.0 M 2-propanol, Figure 4. Furthermore, the decay of the transient absorbance, very small for these limiting conditions, shows a second-order dependence in transient concentration and zero-order dependences in hydrogen ion and 2-propanol concentrations, see Figure 4.

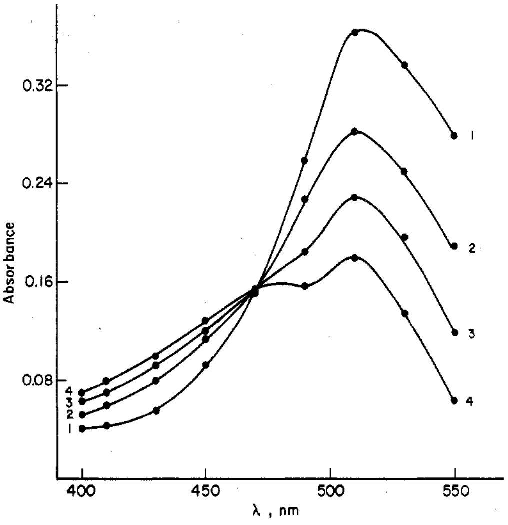

Figure 5. Transient spectrum, generated in flash photolyses of aerated solutions of $[Cu(PTS)]_2^{8-}$ in 10^{-1} M $HClO_4$, obtained at (1) 0 ms, (2) 2 ms, (3) 4 ms, and (4) 6 ms, after the pulse. The flash energy was 250 J/pulse.

These observations show that a new transient species, $Cu(PTSH)^{3-}$ (see Discussion), is formed in addition to the final product $Cu(P\dot{T}S)^{5-}$.

The kind of reactivity, described above for solutions of $[Cu(PTS)]_2^{8-}$ containing 2-propanol, was not observed when 10^{-1}–1.0 M *tert*-butyl alcohol was used as a scavenger.

Oxygen has a large effect upon the reaction course. Flash photolysis was carried out in solutions of $[Cu(PTS)]_2^{8-}$ in 10^{-1} M $HClO_4$ saturated with oxygen under 1 atm. The shape of the transient spectrum changes with time, Figure 5, showing the formation of a new species with λ_{max} ~470 nm. Besides, the decay of the transient absorptions does not produce a permanent modification of the solution spectrum.

The photochemical reactivity of the dimeric copper(II) sulfophthalocyanine was investigated for excitations at various regions of this substrate. Photolyses of deaerated acidic solutions (10^{-1} M $HClO_4$) produced detectable concentrations of intermediates only for irradiations at wavelengths shorter than 290 nm.

The experimental conditions (see below) used in flash photolyses of the monomeric complex $[Cu(PTS)]^{4-}$ were limited by the small concentration of this species that can be reached in aqueous solutions without having a significant association. The irradiation under such conditions produced little, if any, transient absorptions. However, a stable product, formed during the life of the pulse for photolyses of $[Cu(PTS)]^{4-}$ in deaerated solutions containing 10^{-1}–1.0 M 2-propanol, has the same absorption spectrum of the product, $Cu(P\dot{T}S)^{5-}$, obtained in photolyses of alcoholic solutions of the dimeric species (see above and "Continuous Photolysis" section).

Cobalt(II) Sulfophthalocyanine. The dimeric cobalt complex, $[Co(PTS)]_2^{8-}$, was flash photolyzed in deaerated acidic solutions (10^{-1}–10^{-4} M $HClO_4$). The transient spectrum, obtained under such conditions, Figure 1b, is in good agreement with the one reported for cobalt(I) sulfophthalocyanine.[1,3] The rate of the absorption decay presents a good second-order dependence on transient concentration with a ratio $k/\epsilon = (4.0 \pm 0.1) \times 10^4$ cm s^{-1} when such a reaction is followed at λ 480 nm (Figure 2b[22]).

The interception of the intermediates by 2-propanol, used as a scavenger of the oxidized species, was not as efficient as with transients of the copper(II) complex. Transient absorptions were observed only for irradiations in solutions of cobalt(II) sulfophthalocyanine containing large concentrations

Table I. Quantum Yields of the Photochemical Redox Dissociation of Dimeric Copper(II) and Cobalt(II) Sulfophthalocyanines

λ, nm	$10^4 I_0$, einsteins/(L min)	ϕ_d[a]	conditions[b]
		(a) Copper(II) Sulfophthalocyanine	
254	8.3 ± 0.3	$(2.0 \pm 0.2) \times 10^{-3}$	0.1 M $HClO_4$, 2.7 M 2-propanol
254	8.3 ± 0.3	$(1.8 \pm 0.3) \times 10^{-3}$	0.1 M $HClO_4$, 0.5 M 2-propanol
254	8.3 ± 0.3	$(2.4 \pm 0.2) \times 10^{-3}$	1.0 M $HClO_4$, 2.7 M 2-propanol
254	1.0 ± 0.1	$(2.4 \pm 0.3) \times 10^{-3}$	0.1 M $HClO_4$, 0.5 M 2-propanol
254	8.3 ± 0.3	$(2.0 \pm 0.1) \times 10^{-3}$	0.1 M $HClO_4$, 0.5 M 2-propanol, 0.025 M N_2O
254	8.3 ± 0.3	$(2.0 \pm 0.1) \times 10^{-3}$ [c]	0.1 M $HClO_4$, 0.5 M methanol
225	3.0 ± 0.1	0.093 ± 0.002	1.0 M $HClO_4$, 2.7 M 2-propanol
		(b) Cobalt(II) Sulfophthalocyanine	
254	5.0 ± 0.2	$(2.3 \pm 0.3) \times 10^{-3}$	0.1 M $HClO_4$, aerated solution ($[O_2] \simeq 4.2 \times 10^{-4}$ M)
254	5.0 ± 0.2	$(2.1 \pm 0.3) \times 10^{-3}$	0.1 M $HClO_4$, O_2-saturated solution ($[O_2] \simeq 1.4 \times 10^{-3}$ M)
225	3.0 ± 0.1	0.13 ± 0.02	0.1 M $HClO_4$, O_2-saturated solution ($[O_2] \simeq 1.4 \times 10^{-3}$ M)

[a] Quantum yields measured for $[\mathrm{Cu}(\mathrm{P\dot{T}S})]^{5-}$ and $[\mathrm{Co^{II}}(\mathrm{PTS})]^{3-}$, respectively. [b] Solutions deaerated unless specially stated. [c] A quantum yield $\phi = 2.0 \times 10^{-3}$ was obtained for formaldehyde.

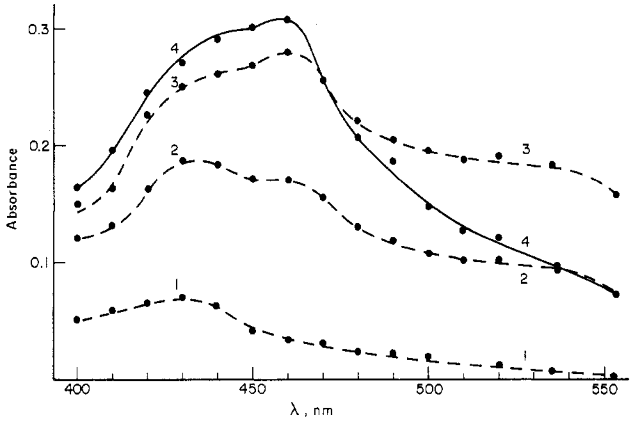

Figure 7. Transient spectrum obtained in flash photolyses of monomeric $[\mathrm{Co}(\mathrm{PTS})]^{4-}$ in deaerated solutions containing 3 M 2-propanol. Curves were obtained at the following reaction times: (1) 0 μs, (2) 200 μs, (3) 1 ms, (4) 10 s.

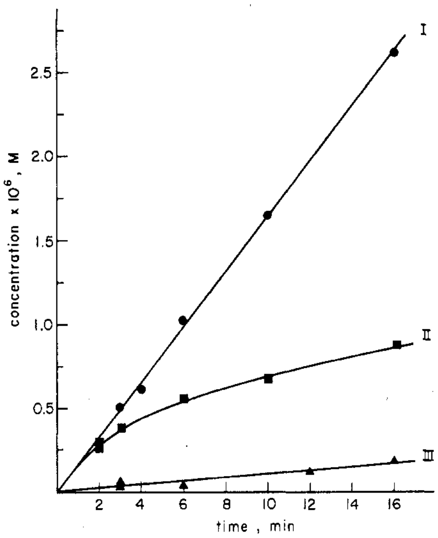

Figure 8. Concentrations of the reduced species, $[\mathrm{Cu}(\mathrm{P\dot{T}S})]^{5-}$, produced for 254-nm photolyses ($I_0 = (8.0 \pm 0.3) \times 10^{-4}$ einstein/(L min)) of $[\mathrm{Cu}(\mathrm{PTS})]_2^{8-}$ in deaerated solutions containing 1 M $HClO_4$ and 1 M 2-propanol: (I) 10^{-4} M, (II) 0.1×10^{-4} M, (III) 0.03×10^{-4} M.

of scavenger ($[(CH_3)_2CHOH] > 1$ M). However, the complex was largely dissociated under these conditions and the observed reaction can not be uniquely assigned to the monomer or the dimer species (see below).

The photochemical reactivity of the monomeric moiety was studied in deaerated acidic (10^{-1} M $HClO_4$) solutions containing a low concentration of the complex ($[[\mathrm{Co}(\mathrm{PTS})]^{4-}] = 10^{-7}$–$10^{-8}$ M) and 2-propanol ($0 \leq [(CH_3)_2CHOH] \leq 5$ M). Transient absorptions were produced only in solutions containing 2-propanol in concentrations larger than 1.0 M, see Figure 6.[22] Moreover, the spectrum of the species, produced during the flash life, transforms by means of a second-order reaction into a long-lived intermediate, Figures 6[22] and 7. A ratio of the second-order rate constant to the extinction coefficient, $k/\epsilon = (2.0 \pm 0.3) \times 10^5$ cm s^{-1}, was obtained for measurements at 430 nm. The transformation of the long-lived intermediate to the final product, Figures 6[22] and 7, presents a first-order dependence on the long-lived species concentration. A rate constant, $k = 4.4 \pm 0.3$ s^{-1}, was obtained for such a decay followed at 535 nm.

The photochemical reactivity of the cobalt(II) sulfophthalocyanine monomeric and dimeric species was investigated under the general conditions indicated above. No transients were produced with detectable yields for excitations of wavelengths longer than 300 nm.

2. Continuous Photolysis. Copper(II) Sulfophthalocyanine. Continuous photolyses of the dimeric copper(II) sulfophthalocyanine were carried out in acidic (10^{-1} M $\geq [HClO_4] \geq 10^{-6}$ M) deaerated solutions. Permanent photochemical transformations were not observed under such conditions for excitations at various wavelengths (225, 254, 320, and 600 nm). Neither $\mathrm{Cu(aq)}^{2+}$ nor open-cycle complexes were detected in irradiated solutions. However, 225- or 254-nm photolyses of the complex in deaerated solutions containing 2-propanol (10^{-3} M $\leq$ [2-propanol] $\leq 10^{-1}$ M; $[HClO_4] = 0.1$ M) did form a stable product. The infrared and visible absorptions of the product ($\lambda_{max} \sim 500$ nm and $\lambda_{max} \sim 950$ nm) show that it is the same copper(II)–ligand radical, $\mathrm{Cu}(\mathrm{P\dot{T}S})^{5-}$, observed in flash irradiations (see above). Other species were formed if the conversion was extended to more than 2–3%. This was observed as a gradual broadening of the initially formed absorption bands and departure from a linear relationship between product concentration and irradiation time.

The depletion of the dimer during photolyses produces also a gradual departure from the linear behavior (Figure 8). Indeed, such deviations seem to be more rapidly noticeable when experimental conditions favor the shift of the dimer–monomer equilibrium toward the monomeric species, see Figure 8.

The dependence of the copper(II)–ligand radical yield on excitation wavelength is shown in Table I. These results are in good agreement with observations made by means of flash photolyses (see above).

Photolyses of $[\mathrm{Cu}(\mathrm{PTS})]_2^{8-}$ were also carried out in solutions deaerated and saturated with N_2O. The results obtained with N_2O and N_2 do not present significant differences between them; see Table I.

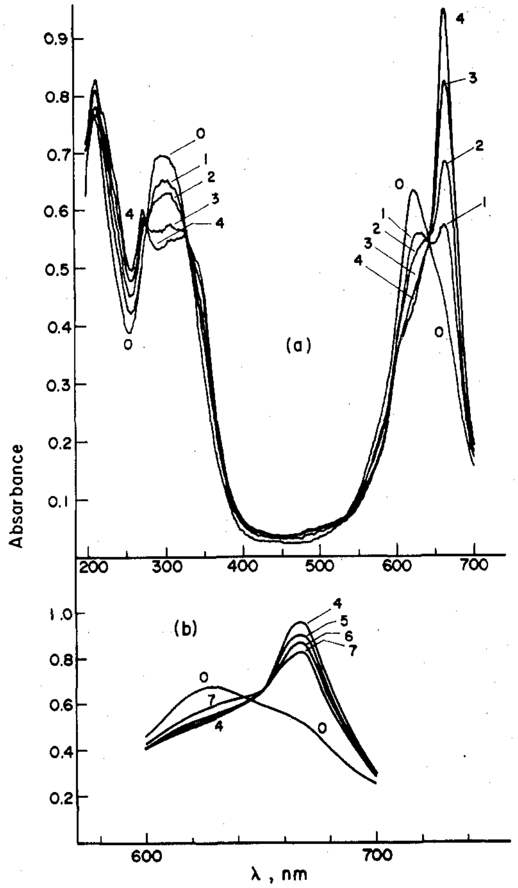

Figure 9. Photolysis of aerated solutions of $[Co(PTS)]_2^{8-}$ in 10^{-1} M $HClO_4$: (a) transformations of the absorption spectrum, measured in a 1-mm optical path length cell, produced with (0) 0-min, (1) 5-min, (2) 10-min, (3) 15-min, and (4) 20-min irradiations at 254 nm ($I_0 = (8.0 \pm 0.3) \times 10^{-4}$ einstein/(L min)); (b) decay of the metastable product produced by 20-min irradiation at 254 nm (see a) and decay after the end of the irradiation period at (5) 20 min, (6) 40 min, and (7) 720 min.

Cobalt(II) Sulfophthalocyanine. Dimeric $[Co(PTS)]_2^{8-}$ did not show the same photochemical reactivity of the copper(II) complex. The absorption spectra of the deaerated solutions (made in 0.1 M $HClO_4$ and 0.1–0.01 M 2-propanol) did not change when they were irradiated at 254 nm ($I_0 \approx 8.0 \times 10^{-4}$ einstein/(L min)) for large periods of time (~3 h). However, photolyses produced noticeable changes in the absorption spectrum when solutions were not properly deaerated.

Photolyses of the dimeric species were carried out in acidic solutions (0.1 M $HClO_4$) saturated with oxygen under 1 atm. The spectra of irradiated samples presented marked modifications compared with those of blanks kept in the dark as indicated in Figure 9. The most noticeable difference was a new absorption band at 660 nm whose intensity was too large to be accounted for by a mixture of dimeric and monomeric Co(II) and Co(III) complexes, Figure 9. The decay of these absorptions was followed at 660 nm for various concentrations of the product species, obtained by irradiation at 254 nm for distinct periods of time and parent complex concentrations ($[Co(PTS)]_2^{8-} = 8 \times 10^{-4}$, 3×10^{-4}, and 2.0×10^{-4} M). These experiments proved that this reaction presents a first-order dependence in transient concentration and zero order dependence in Co(II) complex. An average rate constant value, $k = (2.2 \pm 0.1) \times 10^{-4}\ s^{-1}$, was obtained in these determinations.

Analyses of open-cycle products and/or $Co(aq)^{2+}$ rendered negative results showing that in any of the conditions, indicated above, more than 90% of the products remain as cyclic complexes. Quantum yields were estimated from the depletion of the absorbance at 320 and 620 nm and the positive increments at 660 nm (see Figure 9) at the end of the reaction with O_2.

Discussion

The results indicated above show that redox pathways are available in the photochemistry of the copper(II) and cobalt(II) sulfophthalocyanines in aqueous solutions.

A redox dissociation into radicals can be formulated for the primary reaction of dimeric copper(II) sulfophthalocyanine, eq 1. The recombination of these radicals, eq 2, is able to restore the system to its initial condition in the absence of scavengers. Moreover, the interceptions of the oxidized species $[Cu(PTS)]^{3-}$ with methanol or 2-propanol leave the reduced radical $[Cu(P\dot{T}S)]^{5-}$ as a stable product and a transient, $[Cu(PTSH)]^{3-}$, which is different from the monomeric species $[Cu(PTS)]^{4-}$. It seems that reactions between the oxidized radical $[Cu(P\dot{T}S)]^{3-}$ and alcohols must be regarded as hydrogen abstractions, eq 3, rather than electron transfer to the ligand.[23] Indeed, the absence of this kind of reactivity with *tert*-butyl alcohol suggests that such a reaction occurs with an α-hydrogen as indicated in eq 3. The transformation of the $[Cu(PTSH)]^{3-}$ species can be produced through reactions 5–8. Reaction 8 is the dimerization of the monomeric copper(II) sulfophthalocyanine. However, the lower absorptivities of the monomeric species $Cu(PTS)^{4-}$ show that the absorption decay cannot be justified only by reaction 8. Besides, we have observed that the initial concentration of $[Cu(PTSH)]^{3-}$ and its second-order decay are independent of the acid concentration. These results suggest that equilibrium 5 must be largely displaced toward the protonated species. Therefore, the hydrogen atom should be forming a weakly dissociable bond, with an acid dissociation constant $K_a < 10^{-5}$, in the metastable product $[Cu(PTSH)]^{3-}$.

$$[Cu(PTS)]_2^{8-} + h\nu \rightarrow [Cu(P\dot{T}S)]^{5-} + [Cu(P\dot{T}S)]^{3-} \quad (1)$$

$$[Cu(P\dot{T}S)]^{5-} + [Cu(P\dot{T}S)]^{3-} \rightarrow [Cu(PTS)]_2^{8-} \quad (2)$$

$$[Cu(P\dot{T}S)]^{3-} + (CH_3)_2CHOH \rightarrow [Cu(PTSH)]^{3-} + (CH_3)_2\dot{C}OH \quad (3)$$

$$2(CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \quad (4)$$

$$[Cu(PTSH)]^{3-} \rightleftharpoons [Cu(PTS)]^{4-} + H^+ \quad (5)$$

$$2[Cu(PTSH)]^{3-} \rightarrow [Cu(PTS)]_2^{8-} + 2H^+ \quad (6)$$

$$[Cu(PTSH)]^{3-} + [Cu(PTS)]^{4-} \rightarrow [Cu(PTS)]_2^{8-} + H^+ \quad (7)$$

$$2[Cu(PTS)]^{4-} \rightarrow [Cu(PTS)]_2^{8-} \quad (8)$$

The photochemical behavior of the dimeric cobalt(II) sulfophthalocyanine differs from that observed with the similar copper(II) complex. The reduced transient species, because of the absorptions at 480 and 460 nm, is clearly the cobalt(I) sulfophthalocyanine complex reported by other authors.[1,3] Moreover, the oxidized partner cannot be a ligand radical and should be considered as a cobalt(III)–phthalocyaninetetrasulfonic acid complex. A radical resulting from the oxidation of the ligand is expected to have absorptions at λ ~500 nm.[7] Such a contribution to the transient absorption was not observed. In addition, the absence of any tendency to abstract hydrogen atoms from alcohols constitutes a marked departure of the behavior observed with copper(II) sulfophthalocyanine oxidized radical, $Cu(P\dot{T}S)^{3-}$ in eq 3. In this regard, the primary process of the dimeric cobalt(II) sulfophthalocyanine can be formulated as a photodissociation into Co(I) and Co(III) species, as indicated in eq 9. The recombination

$$[Co(PTS)]_2^{8-} + h\nu \rightarrow [Co^I(PTS)]^{5-} + [Co^{III}(PTS)]^{3-} \quad (9)$$

$$[\mathrm{Co^I(PTS)}]^{5-} + [\mathrm{Co^{III}(PTS)}]^{3-} \rightarrow [\mathrm{Co(PTS)}]_2{}^{8-} \qquad (10)$$

reaction, eq 10, confers photoreversibility to this system but only under limited conditions. Indeed, the interception of $[\mathrm{Co^I(PTS)}]^{5-}$ with oxygen produces a metastable species, and the final reaction product can be assigned as a cobalt(III) sulfophthalocyanine complex. Moreover, this behavior, transformation into a stable product, contrasts with that presented by copper(II)–ligand radical intermediates trapped with oxygen. Formations of peroxo and superoxo complexes have been found in reactions of oxygen with cobalt(II) complexes.[24–27] In this regard, eq 11–13 may be a feasible

$$[\mathrm{Co^I(PTS)}]^{5-} + \mathrm{O_2} \rightarrow [\mathrm{Co(PTS)(O_2)}]^{5-} \qquad (11)$$

$$[\mathrm{Co(PTS)(O_2)}]^{5-} + [\mathrm{Co(PTS)}]^{4-} \rightleftharpoons [(\mathrm{Co(PTS)})_2(\mathrm{O_2})]^{9-} \qquad (12)$$

$$[(\mathrm{Co(PTS)})_2(\mathrm{O_2})]^{9-} \xrightarrow[2\mathrm{H^+}]{} [\mathrm{Co^{II}(PTS)}]^{4-} + \mathrm{H_2O_2} + [\mathrm{Co^{III}(PTS)}]^{3-} \qquad (13)$$

explanation of the reactivity observed between oxygen and cobalt(II) sulfophthalocyanine intermediates. Adducts between oxygen and the copper(II) sulfophthalocyanine are also formed, Figure 5. However, the different nature of the metal centers, a reducing Co(I) and a stable Cu(II), respectively, suggests that oxygen is attached to the ring in the case of the copper(II)–radical complex. Moreover, the absence of a final product indicates that such intermediates, the peroxo derivative and the oxidized Cu(II) ligand radical, are able to react closing a reaction cycle, as it is indicated in eq 1 and 2 and 14 and 15.

$$[\mathrm{Cu(P\dot{T}S)}]^{5-} + \mathrm{O_2} \rightarrow [\mathrm{Cu(P\dot{T}S{-}O_2)}]^{5-} \qquad (14)$$

$$[\mathrm{Cu(P\dot{T}S{-}O_2)}]^{5-} + [\mathrm{Cu(P\dot{T}S)}]^{3-} \rightarrow [\mathrm{Cu(PTS)}]_2{}^{8-} + \mathrm{O_2} \qquad (15)$$

The photoredox behavior of the dimeric copper(II) and cobalt(II) sulfophthalocyanines is observed only for excitations at energies larger than 105 kcal/mol (260 nm). This might be interpreted as a photochemical reaction produced in some excited state of the dimers. Such a state may involve an intermolecular redistribution of charge between units of the dimer, namely, a charge-transfer state. However, it is also feasible that the photoreactive state, mainly localized in one unit of the dimer, is a stronger oxidant than the ground state. In such a case, the charge-transfer process should be a reaction that follows the population of this state. This possibility gains some further support from the observed photochemical redox reactivity of the monomeric species.

Our experimental results show that the upper excited states of the monomeric copper(II) and cobalt(II) sulfophthalocyanines, indicated as $*[\mathrm{Co^{II}(PTS)}]^{4-}$ in eq 16–18, behave as

$$[\mathrm{Co^{II}(PTS)}]^{4-} + h\nu \xrightarrow{\phi} *[\mathrm{Co^{II}(PTS)}]^{4-} \qquad (16)$$

$$*[\mathrm{Co^{II}(PTS)}]^{4-} \rightarrow [\mathrm{Co^{II}(PTS)}]^{4-} \qquad (17)$$

$$*[\mathrm{Co^{II}(PTS)}]^{4-} + \mathrm{(CH_3)_2CHOH} \rightarrow [\mathrm{Co^{II}(P\dot{T}SH)}]^{4-} + \mathrm{(CH_3)_2\dot{C}OH} \qquad (18)$$

$$2[\mathrm{Co^{II}(P\dot{T}SH)}]^{4-} \rightarrow [\mathrm{Co(PTS)}]_2{}^{10-} + 2\mathrm{H^+} \qquad (19)$$

$$[\mathrm{Co(PTS)}]_2{}^{10-} \rightarrow 2[\mathrm{Co^I(PTS)}]^{5-} \qquad (20)$$

oxidants.[28] Moreover, this behavior can be represented by eq 16, 18, 4, 19, and 20 for cobalt(II) sulfophthalocyanine. Reactions 16–18 must be regarded as fast processes for the time resolution of conventional flash photolysis.[29] However, the transformation of the cobalt(II)–ligand radical into the dimeric species, eq 19, is sufficiently slow for observation in our experimental conditions ($k/\epsilon = (2.0 \pm 0.3) \times 10^5$ cm s^{-1}). The last step of this reaction mechanism, eq 20, is very slow, $k = 4.4 \pm 0.1$ s^{-1}. This value is consistent with reported rate constants for the dissociation of dimeric sulfophthalocyanines.[31]

The photochemical behavior of the monomeric copper(II) sulfophthalocyanine can be also explained by reactions similar to those proposed for the cobalt(II) system. However, the large stability of the reduced radical prevents any further transformation into Cu(I) species.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1858 from the Notre Dame Radiation Laboratory.

Registry No. $[\mathrm{Co(PTS)}]^{4-}$, 67462-30-0; $[\mathrm{Cu(PTS)}]^{4-}$, 67462-31-1; 2-propanol, 67-63-0; methanol, 67-56-1; *tert*-butyl alcohol, 75-65-0.

Supplementary Material Available: Figure 2 showing the dependence of the half-life on transient concentration and Figures 3 and 6 containing oscillographic traces (3 pages). Ordering information is given on any current masthead page.

References and Notes

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(14) Ligand abbreviations: $\mathrm{(PTS)}^{6-}$, phthalocyaninetetrasulfonate hexaanion; $\mathrm{(P\dot{T}S)}^{5-}$, one-electron-oxidized radical; $\mathrm{(P\dot{T}S)}^{7-}$, one-electron-reduced radical; $\mathrm{(PTSH)}^{5-}$, hydrogenated derivative with the same oxidation state of $\mathrm{(PTS)}^{6-}$.
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