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## Photochemistry of Transition-Metal Phthalocyanines. Mechanistic Aspects of the Photochemistry of the Acido(phthalocyanine)rhodium(III) Complexes Investigated by Continuous, Flash, and Laser Flash Photolysis

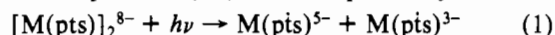
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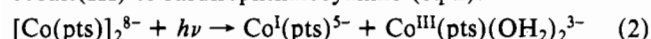
Rh(ph)(CH<sub>3</sub>OH)X, X = Cl, Br, or I, have been prepared and characterized. Continuous-wave irradiations of these phthalocyanines in the ultraviolet region of the spectrum, in acetonitrile and acetonitrile-isopropyl alcohol mixtures, result in the redox-induced substitution of the axially coordinated halide ions by the solvent. Even though the overall reaction was photosubstitution, the intermediates observed by conventional and laser flash photolysis were found to be rhodium(II) phthalocyanine and rhodium(III) phthalocyanine ligand radicals. The photoredox processes were attributed to the population of ( $n\pi^*$ ) ligand-centered excited states that involve the lone electron pair from the bridge nitrogens of the phthalocyanine ligand.

### Introduction

The optical spectra of the transition-metal phthalocyanines are rich in intense absorptions.<sup>4</sup> A large contribution to the absorption spectra is made by ligand-centered  $\pi\pi^*$  transitions.<sup>3-5</sup> However, phthalocyanine to metal and metal to phthalocyanine charge-transfer transitions have been reported for a number of phthalocyanines.<sup>6-8</sup> In addition, ligand-centered  $n\pi^*$  states also make contributions to the UV-vis spectra and they seem to be responsible, in some cases, for the photochemical properties of these compounds.<sup>9,10</sup> Several studies on the photochemistry of transition-metal phthalocyanines have been recently reported.<sup>4,9-15</sup> The tetrasulfophthalocyanines of various metals, namely, M(pts)<sup>4-</sup> with M = Cu(II), Co(II), or Fe(II) and Co(pts)(OH<sub>2</sub>)<sub>2</sub><sup>3-</sup>, form dimeric and monomeric species in aqueous solutions.<sup>10,16,17</sup> Irradiations of the dimers in the ultraviolet bands induce distinctive redox processes that are determined by the metal center. Indeed, the photodissociation into ligand radicals, eq 1, has been observed in ultraviolet irradiations of the dimeric copper(II), iron(II) and diaquocobalt(III) tetrasulfophthalocyanines.<sup>9,10</sup>

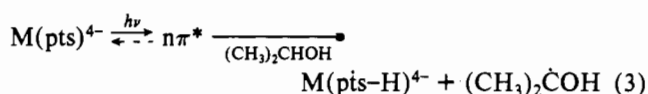


A photoinduced dissociation into metal oxidized and metal reduced species has been observed in photolyses of the dimeric cobalt(III) tetrasulfophthalocyanine (eq 2).<sup>10</sup>



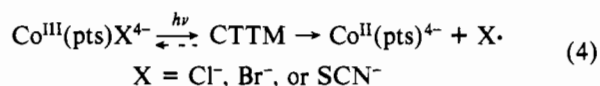
The processes indicated above, eq 1 and 2, have been related to the population of either ligand-centered  $n\pi^*$  states or excited states involving charge transfer between units of the dimer.<sup>10</sup> Also the photoreactivity of the monomeric species can be

explained if one assumes that the  $n\pi^*$  excited states are photoreactive. Indeed, irradiations of the monomeric tetrasulfophthalocyanines of cobalt(II) and copper(II) induce the abstraction of hydrogen from appropriate donors (eq 3).<sup>9</sup>



Some of these reactions (eq 1-3) could probably be involved in the photoenhancement of the catalytic activity of cobalt(II) tetrasulfophthalocyanine in the oxidation of mercaptoethanol.<sup>18</sup> However, the direct participation of excited states is suggested by the existence of  $\pi\pi^*$  excited states with nanosecond lifetimes<sup>19,20</sup> and/or the possible existence of reactive charge-transfer states.<sup>8,11</sup>

Another class of photoreactions was observed with acido-(tetrasulfophthalocyanine)cobalt(III) complexes, acido = Cl<sup>-</sup>, Br<sup>-</sup>, or SCN<sup>-</sup>. These complexes are monomeric in aqueous solutions and exhibit photochemical transformations that are characteristic of the charge-transfer to metal, CTTM, excited states (eq 4).<sup>10</sup> The differences between the photochemical



behavior of the acido complexes (eq 4) and the monomeric cobalt(II) and copper(II) tetrasulfophthalocyanines (eq 3) suggest that the acido to cobalt(III) charge-transfer states are placed at lower energies than the reactive ligand-centered  $n\pi^*$  state in the other phthalocyanines. The energies of the acido to metal charge-transfer states are expected to depend on the redox properties of the metal center.<sup>21,22</sup> In this regard it is interesting to compare the photochemistries of isoelectronic complexes, e.g., rhodium(III) and cobalt(III) phthalocyanines. Monomeric acido(phthalocyanine)rhodium(III) complexes, acido = Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>, have been obtained in this work. The photochemical properties, reported here, can be associated with the population of ligand-centered  $n\pi^*$  excited states.

### Experimental Section

**Photochemical Procedures.** Continuous-wave irradiations at 254 nm were carried out with low-pressure mercury lamps. A Rayonet lamp, placed in a Merry Go Round minireactor, or a U-shaped GE

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- (1) Parts of this work were presented as a prerequisite for the B.S. degree of Kalamazoo College.
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4T4 lamp were used for 254-nm photolyses under different geometrical configurations.<sup>23</sup> A high-pressure xenon lamp, 300 W Vix UV Eimac Illuminator, coupled with a high-intensity monochromator and collimating lenses was used for quasi-monochromatic visible and ultraviolet irradiations. Relative values of the high intensity were measured with a thermopile microvoltmeter apparatus. The absolute values were determined with tris(oxalato)ferrate(III).<sup>24</sup> Routine checks of the intensity at wavelengths shorter than 300 nm were carried out with  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ .<sup>25</sup> The concentrations of the photolytes were adjusted in order to absorb more than 99.99% of the incident light.

The apparatus used for laser flash photolysis was previously described.<sup>26</sup> A Molecron 400 nitrogen laser was used for the 337-nm excitation of the complexes. A 150-W high-pressure xenon lamp, pulsed to around  $10^4$  times the steady-state power, was used as a source for monitoring the transients. The synchronization of the various events, excitation and monitoring of the transients, and the treatment of the data were carried out on a PDP-11 computer.

Two FP-8-100C Xenon Corp. flash lamps, connected in series, were fired at energies between 250 and 40 J/pulse in our flash photolysis experiments.<sup>27</sup> A lifetime of 30  $\mu\text{s}$  was measured for the light pulse under these conditions. Hence points for either kinetics or spectral determinations were regarded significant for sampling times equal to or longer than 50  $\mu\text{s}$ . The raw data, stored in a digital form in a Biomation 805 waveform recorder, were processed in a Digital PDP-8L computer in order to obtain either rate constants or spectral information. Appropriate cutoff filters were used for the irradiation of the photolytes at preselected wavelengths.

The intermediates' ESR spectra were determined with a Varian spectrometer. The solutions, thermostated at room temperature, were irradiated in the cavity of the spectrometer. A constant flow of the liquid ensured the refreshing of the solution in the cavity.

Streams of Ar were used for the deaeration of the solutions. Also, vacuum deaeration was used for those experiments where gaseous products were investigated.

**Analytical Procedures.** Chloride, bromide, and iodide ions were analyzed with HNU ion-selective electrodes. Irradiated solvents and blanks were diluted with a  $\text{NaNO}_3$  solution in order to adjust the ionic strength to 0.1 M. A differential procedure was used whenever the analysis demanded to measure ion concentrations in regions where the electrodes exhibit a low sensitivity. A known concentration of the halide was added to the blank and irradiated solutions in order to bring an appropriate sensitivity to the electrodes. The difference in the redox potentials of the solutions, prepared with the sample and the blank, was associated with the additional concentration of halide produced during photolyses.

The redox equivalents of the phthalocyanines were determined by following the procedure of Elvidge.<sup>28</sup> A given amount of the complex was dissolved in sulfuric acid, and an excess of dichromate was added to the solution. The solution was maintained at 60 °C for 1/2 h and then brought to room temperature. The excess dichromate was titrated with  $\text{Fe}^{2+}(\text{aq})$ . The redox titration was followed with a polarized Pt electrode vs. a calomel electrode.

Elemental analyses were carried out according to procedures reported elsewhere.<sup>29</sup> Hydrogen gas was analyzed by gas chromatography. The gas was removed under vacuum from the irradiated samples. The procedure was standardized with known amounts of hydrogen.

**Materials.** The bisulfate complex  $[\text{Rh}(\text{ph})(\text{OH}_2)_2]\text{SO}_4\text{H}$  was obtained by procedures reported in the literature.<sup>30</sup> Although an 80% yield was reported for such a preparation, we found that the actual yield is highly erratic and small, namely, close to 10%. Part of the temperamental behavior of the preparation seems to be associated with adventitious impurities in the commercially available  $\text{RhCl}_3$ . The acido derivatives  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{X}$ , with  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , were obtained by anation of the diaquo complex with 5–10 times molar

Table I. Elemental Analysis and Redox Equivalents of Transition-Metal Phthalocyanines

complex	atoms of O consumed		oxidn state of metal	% S, Cl, Br, or I	
	found	calcd		found	calcd
$\text{Rh}(\text{ph})(\text{H}_2\text{O})_2\text{HSO}_4$	1.25	1.5	+3	4.4	4.7
$\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Cl}$	1.40	1.5	+3	5.8	5.2
$\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$	1.43	1.5	+3	10.6	11.0
$\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{I}$	1.44	1.5	+3	16.7	16.4
$\text{Cu}(\text{ph})^a$	0.87	1.0	+2		
$\text{Na}_4\text{Cu}(\text{pts})^a$	0.89	1.0	+2		

<sup>a</sup> These complexes were used to standardize the titration procedure. Commercially obtained samples were recrystallized three times and used for the titrations.

excess of the sodium halides. Solutions of  $\text{Rh}(\text{ph})(\text{OH}_2)_2^+$  and a given sodium halide in methanol were refluxed at  $65 \pm 5$  °C for 2 h. The solvent was evaporated under vacuum until the formation of a solid precipitate. Such a crude product was placed under vacuum at 50 °C for at least 12 h and then was recrystallized several times from methanol. Analyses reported below (see Results) show the nature and purity of the complexes.

Aldrich spectral quality acetonitrile was distilled in an all-glass apparatus provided with a 40-theoretical-plate fractionating column. The distillate was dried over molecular sieve. Other chemicals were analytical grade and used without further purification.

## Results

**Structure of the Rhodium(III) Phthalocyanines:** Elemental analyses of the Rh(III) complexes reveal the presence of one anion,  $\text{X} = \text{SO}_4\text{H}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , per rhodium (Table I). These results are in good agreement with determined redox equivalents (Table I). Such equivalents demonstrate that the rhodium is in a tripositive oxidation state.

Absorption bands that are characteristic of coordinated methanol were observed in the infrared spectra of these compounds.<sup>31–33</sup> Moreover, potentiometric measurements indicate that the anions,  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , are strongly coordinated to the metal. Such measurements, carried out with solutions of the complexes in acetonitrile, revealed a concentration of free halides beyond the detection limit of the electrodes, i.e., less than 0.1% of the Rh(III) concentration. These observations suggest that the halides are axially coordinated to the Rh(III) center forming complexes with a structure, I, similar to that previously proposed for another rhodium(III) phthalocyanine<sup>34</sup> and related rhodium(III) porphyrins.<sup>35</sup>

The UV-vis absorption spectra of the rhodium(III) phthalocyanines were determined at various complex concentrations and medium conditions. The near-infrared absorbances, e.g.,  $\lambda_{\text{max}} \approx 650$  nm, exhibited an almost linear dependence on complex concentration. A small departure from linearity, observed for concentrations larger than  $10^{-3}$  M in acetonitrile, show that the acido(phthalocyanine)rhodium(III) ions mainly exist as monomeric species under these conditions, i.e., more than 95% of the Rh(III) is in a monomeric form. The addition of various solutes to the acetonitrile solutions, namely,  $10^{-1}$  M  $\text{NaClO}_4$ , 2 M 2-propanol, or 1 M  $\text{H}_2\text{O}$ , have little effect on the dimerization process, which remains negligible. Moreover, the absorption spectra of the monomers exhibited the general features reported for other phthalocyanines (Figure 1).<sup>4,5,10</sup> Differences between the spectra of the complexes  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{X}$ , with  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ ,

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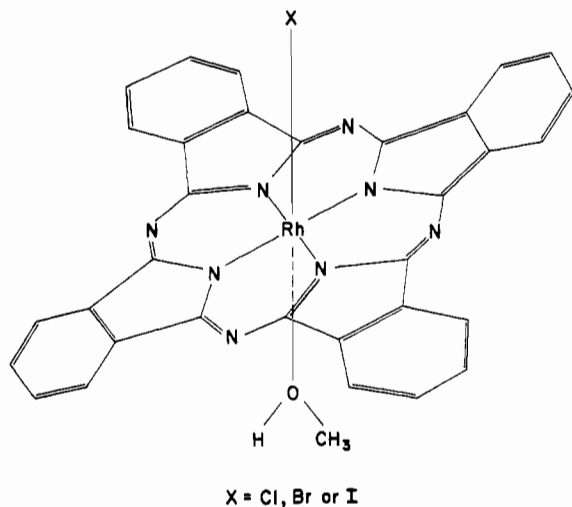
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and  $\text{Rh}(\text{ph})(\text{OH}_2)_2^+$  can be attributed to the presence of either new charge-transfer transitions or perturbations introduced by the axial ligands or both.

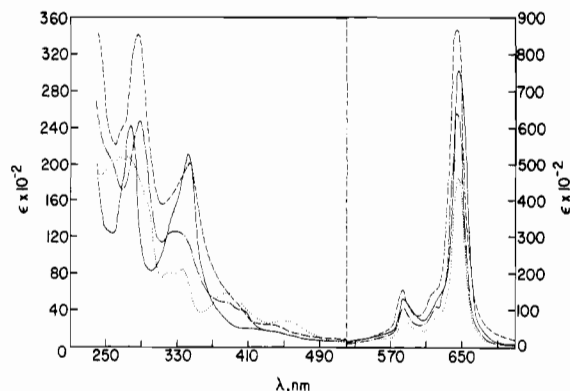
The acido complexes undergo a very slow thermal solvation in acetonitrile with less than 1% of the acido ligand substituted in 24 h. Indeed, the rates of these thermal processes are comparable to those reported for other Rh(III) complexes.<sup>35,36</sup>

**Photolysis Products.** Monochromatic irradiations of bromo(phthalocyanine)rhodium(III),  $\lambda_{\text{excit}} \leq 450$  nm, in deaerated acetonitrile induce the solvolysis of the bromide ligand. The solvated product, assigned as  $\text{Rh}(\text{ph})(\text{CH}_3\text{CN})_2^+$ , was characterized by means of the spectral changes produced in these irradiations (Figure 2) and the known spectra of various rhodium(III) phthalocyanines. In addition, photolyses of the bromide complex in water-acetonitrile mixtures, namely, 1.0–10.0%  $\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ , form the aqueous complexes,  $\text{Rh}(\text{ph})(\text{OH}_2)_2^+$  (Figure 2).

Bromide ions were detected as photolysis products in either pure acetonitrile or water-acetonitrile mixtures. The photo-substitution products  $\text{Br}^-$  and  $\text{Rh}(\text{ph})(\text{solvent})_2^+$ , where solvent is  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{CN}$ , were formed in a 1:1 stoichiometric relationship (Table II).

The other members of the series, namely  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Cl}$  and  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{I}$ , undergo similar photochemical transformations. Moreover, all the acido complexes seem to experience a secondary photolysis, which produces a mixture of products. Such a behavior, observed for conversions to products larger than 10%, introduce complications in the evaluation of quantum yields from spectral data.

**Product Yields.** The formation of the photochemical products was investigated by irradiating for different periods. Linear plots of the product concentration vs. irradiation time were obtained for small conversions to products (Figure 3). However, strong departures from linearity were observed for conversions to products larger than 10% (Figure 3). Such a photochemical behavior demanded that product yields were determined for conversions to products smaller than 10% and/or were extrapolated to a zero irradiation time. The yields, obtained for 254-nm excitations, show a large dependence on medium conditions (Table II and Figure 4). Part of this dependence can be traced to the scavenging of reactive intermediates by added substrates (Figure 4). Trace amounts of hydrogen were produced under various experimental conditions.



**Figure 1.** Absorption spectra of acido(phthalocyanine)rhodium(III) complexes in acetonitrile: (—)  $\text{Rh}(\text{ph})(\text{OH}_2)_2^+$ ; (---)  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Cl}$ ; (····)  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$ ; (-·-·)  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{I}$ .

**Table II.** Quantum Yields for the Solvolysis of the Acido-rhodium(III) Phthalocyanines in 254-nm Photolyses<sup>a</sup>

medium conditions <sup>b</sup>	$\phi \times 10^2$	
	$\Delta D^c$	$X^d$
<b>Rh(ph)(CH<sub>3</sub>OH)Cl</b>		
100% CH <sub>3</sub> CN		2.3 ± 0.2
20% H <sub>2</sub> O, 80% CH <sub>3</sub> CN	7.0 ± 0.5	8.0 ± 0.5
20% 2-propanol, 80% CH <sub>3</sub> CN	6.6 ± 0.7	6.7 ± 0.7
10 <sup>-1</sup> M NaClO <sub>4</sub> in 20% H <sub>2</sub> O and 80% CH <sub>3</sub> CN	3.0 ± 0.5	2.8 ± 0.3
<b>Rh(ph)(CH<sub>3</sub>OH)Br</b>		
100% CH <sub>3</sub> CN		1.4 ± 0.1
20% H <sub>2</sub> O, 80% CH <sub>3</sub> CN		6.0 ± 0.2
20% 2-propanol, 80% CH <sub>3</sub> CN		6.8 ± 0.6
10 <sup>-1</sup> M NaClO <sub>4</sub> in 20% H <sub>2</sub> O and 80% CH <sub>3</sub> CN		5.3 ± 0.5
<b>Rh(ph)(CH<sub>3</sub>OH)I</b>		
100% CH <sub>3</sub> CN		1.4 ± 0.1
20% 2-propanol, 80% CH <sub>3</sub> CN		6.0 ± 0.3

<sup>a</sup> Experiments carried out with a light intensity,  $I_0 = (1.9 \pm 0.2) \times 10^{-4}$  einstein/(L min). <sup>b</sup> Solutions deaerated with Ar streams.

<sup>c</sup> Quantum yields determined by means of the spectral changes.

<sup>d</sup> Quantum yields determined by direct measurements of the free halides.

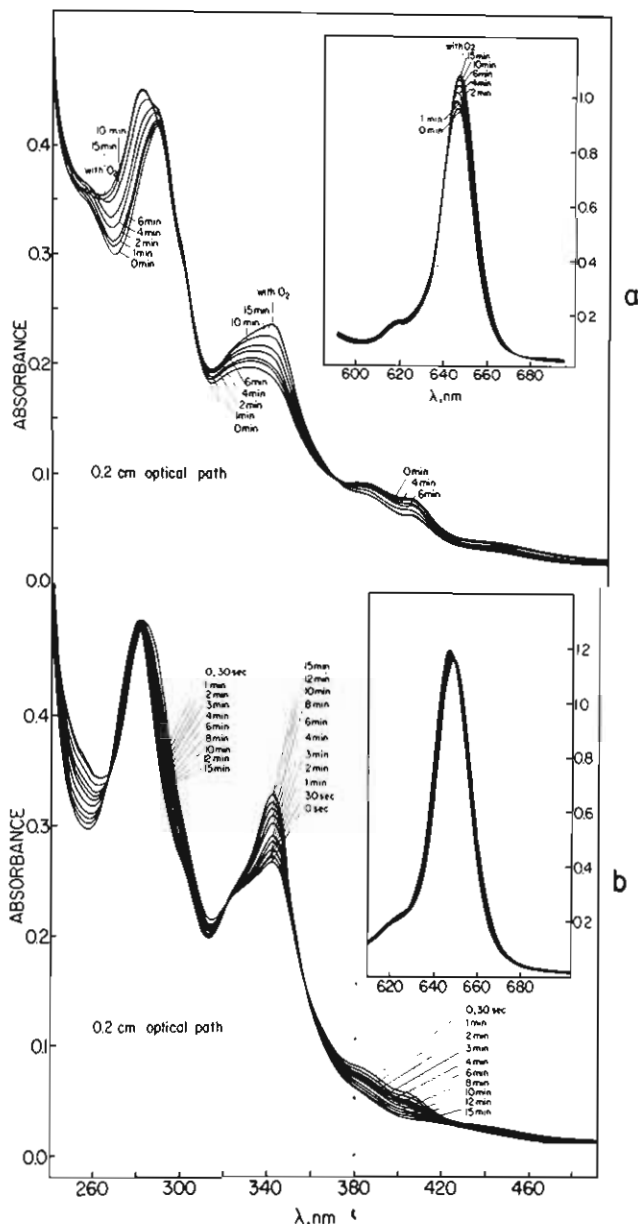
**Table III.** Rate Constants of Transients Generated in Laser Flash Photolysis of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}^d$

medium conditions <sup>b</sup>	$k_0 \times 10^{-6}$ , s <sup>-1</sup>	medium conditions <sup>b</sup>	$k_0 \times 10^{-6}$ , s <sup>-1</sup>
0.0 M NaClO <sub>4</sub>	2.4 ± 0.2	0.07 M 2-propanol	2.6 ± 0.2
0.05 M NaClO <sub>4</sub>	3.1 ± 0.2	0.35 M 2-propanol	3.1 ± 0.2
0.10 M NaClO <sub>4</sub>	3.4 ± 0.3	0.70 M 2-propanol	3.8 ± 0.3
0.50 M NaClO <sub>4</sub>	5.0 ± 0.2	1.50 M 2-propanol	5.1 ± 0.2
1.00 M NaClO <sub>4</sub>	6.7 ± 0.4		

<sup>a</sup> Reaction followed at 510 nm (see also Figure 5). <sup>b</sup> Solutions in deaerated acetonitrile.

**Laser Flash Photolysis.** Laser flash photolysis of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$  in deaerated acetonitrile reveals several transients in a nanosecond time scale (Figure 5).<sup>37</sup> The transient spectrum is produced with  $t_{1/2} \approx 16$  ns after the irradiation (Figure 5). Moreover, the spectrum determined 70 ns after the irradiation exhibited a broad maximum with  $\lambda_{\text{max}} \approx 460$  nm (Figure 5). The decay of the transient produces also a shift of the maximum, namely, to  $\lambda_{\text{max}} \approx 510$  nm (Figure 5). These spectral transformations were attributed, in part, to the formation of the primary species, namely,  $\text{CH}_2\text{CN}^\cdot$  and

(37) Part of the transient behavior in a nanosecond time scale can be related to the decay of low-lying  $\pi\pi^*$  excited states in the iodo complex. The  $\pi\pi^*$  excited states of the chloro and bromo complexes have microsecond lifetimes. The photophysical properties of the rhodium(III) phthalocyanines will be reported elsewhere.<sup>44</sup>



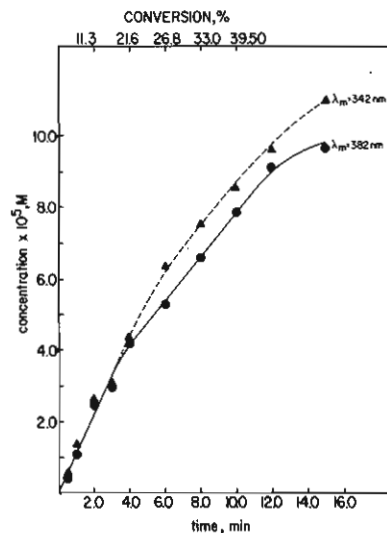
**Figure 2.** Characteristic spectral transformations observed in 254-nm photolyses of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$  in (a) 100%  $\text{CH}_3\text{CN}$  and (b) 10%  $\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ .

$\text{Rh}(\text{ph}-\text{H})(\text{CH}_3\text{OH})\text{Br}$ , from a ligand-centered excited state and to the subsequent reactions of these intermediates.<sup>38</sup>

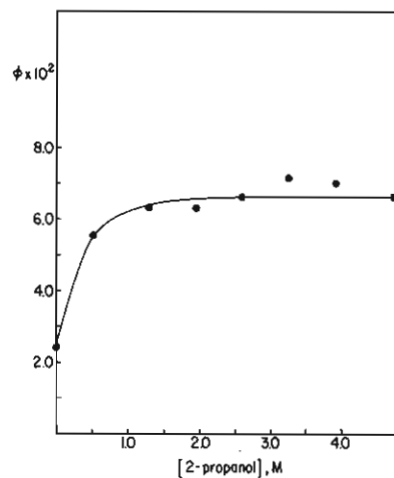
The rate of decay of the transient, followed at 510 nm, exhibited a first-order dependence in transient concentration. However, measurements of the rate constant under various conditions reveal the complexity of such a process (see below and Table III). The time-resolved spectral transformations observed at 580 nm contrast with those observed at 510 nm (Figure 5). A decay of the 580-nm transient with  $t_{1/2} \approx 5.0 \times 10^{-8}$  s exhibited a first-order dependence in transient concentration,  $k = 1.4 \times 10^7 \text{ s}^{-1}$ . Such a decay is followed by a growth of the absorbance at longer reaction times (Figure 5). The rate of the growth presents a first-order dependence in transient and  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$  concentrations with a rate constant  $k = 5.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The assignment of this process to the reaction of  $\text{CH}_2\text{CN}\cdot$  with excess rhodium(III)

(38) Notice that one-electron reduced or oxidized ligand radicals with  $\lambda_{\text{max}}$  within the 500–600-nm region have been previously generated by electrochemical,<sup>13</sup> chemical,<sup>39</sup> and photochemical<sup>9,10</sup> means.

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**Figure 3.** Dependence of the 342- and 382-nm absorbance changes on irradiation time and the conversion to products. Photolyses of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$  in deaerated acetonitrile were carried out with light intensities  $I_0 \approx 10^{-4}$  einstein/(L min).



**Figure 4.** Dependence of the photosolvation yield on 2-propanol concentration. Values were obtained in 254-nm photolyses of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$  in deaerated  $\text{CH}_3\text{CN}$ , with light intensity  $I_0 \approx 10^{-4}$  einstein/(L min).

phthalocyanine was confirmed by scavenging with 2-propanol.

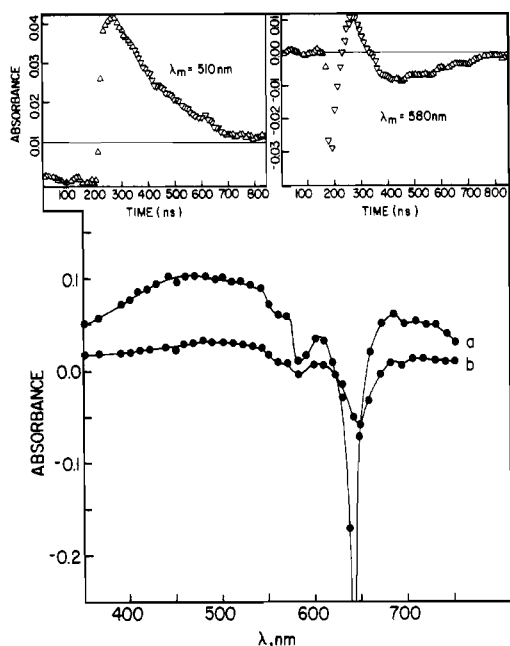
The rate constant for the decay of the 510-nm absorbance was determined at various 2-propanol concentrations (Table III). The dependence of the overall rate constant,  $k_0$ , on 2-propanol concentration can be described by two terms as in eq 5. One term is independent of 2-propanol while the other

$$k_0 = 2.4 \times 10^6 + 1.4 \times 10^6[2\text{-propanol}] \text{ (s}^{-1}\text{)} \quad (5)$$

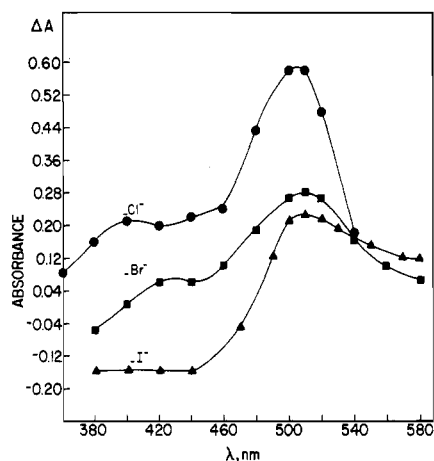
contains a first-order dependence on transient concentration (eq 5). The term with a first-order dependence in 2-propanol concentration has been attributed to scavenging of  $\text{CH}_2\text{CN}\cdot$  radicals by 2-propanol. In addition, the decay shows a marked dependence on the ionic strength (Table III).

The photochemical behavior of the chloro and iodo complexes is qualitatively similar to that reported for the bromide complex.

**Flash Photolysis.** Intermediates with microsecond to second lifetimes were detected by flash photolysis,  $\lambda_{\text{excit}} > 280$  nm. Flash irradiations of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{X}$ , with  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , in deaerated acetonitrile produce difference spectra that show differences originated in the background contributions of the rhodium(III) complexes (Figure 6). These spectra were assigned to a mixture of intermediates, namely, a one-electron



**Figure 5.** Transient observed in laser flash photolysis of Rh(ph)-(CH<sub>3</sub>OH)Br in deaerated CH<sub>3</sub>CN. Spectra determined at (a) 70 ns and (b) 400 ns. The insets show the time dependence of the transients observed at two different wavelengths.

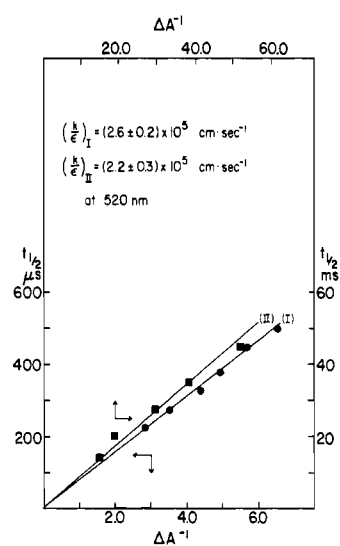


**Figure 6.** Transient spectra observed in flash irradiations of Rh(ph)-(CH<sub>3</sub>OH)X, with X = Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>, in deaerated acetonitrile. Excitations were with 250 J/pulse and  $\lambda_{\text{excit}} \geq 280$  nm.

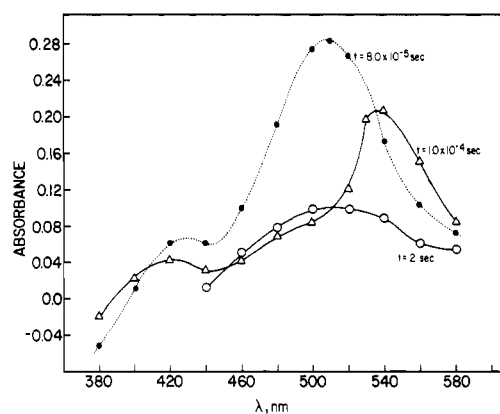
reduced and a one-electron oxidized rhodium(III) ligand radical. Flash irradiations at longer wavelengths, namely,  $\lambda_{\text{excit}} \geq 320$  nm, produce smaller conversions to the same transient spectra that were observed for excitations at shorter wavelengths, namely,  $\lambda_{\text{excit}} \geq 280$  nm.

The observed transient disappeared by a complex process that involves two stages. Each of these stages exhibited a second-order dependence in transient concentration. The ratios of the rate constant to the extinction coefficient obtained for the bromide complex are  $(k/\epsilon)_I = (2.6 \pm 0.5) \times 10^5 \text{ cm s}^{-1}$  and  $(k/\epsilon)_{II} = (2.4 \pm 0.2) \times 10^4 \text{ cm s}^{-1}$  at 520 nm, respectively (Figure 7). Almost the same values were obtained with the other rhodium(III) complexes.

Interception of the intermediates with 2-propanol changes the transient spectra (see above and Figure 7). Indeed, 2-propanol in large concentrations, [2-propanol]  $\geq 1.0$  M, scavenges the CH<sub>2</sub>CN<sup>•</sup> radical and changes the transient spectra to that of the species assigned as reduced rhodium(III) ligand radicals (Figure 8). The very long-lived product with  $t_{1/2} > 3$  s can be tentatively described as a Rh(I) complex (Figure 8).



**Figure 7.** Dependence of the half-lifetime for the transient decay on the 520-nm initial absorbance,  $\Delta A$ , in flash irradiations of Rh(ph)-(CH<sub>3</sub>OH)Br in deaerated acetonitrile. Excitations were with 250 J/pulse and  $\lambda_{\text{excit}} \geq 280$  nm.

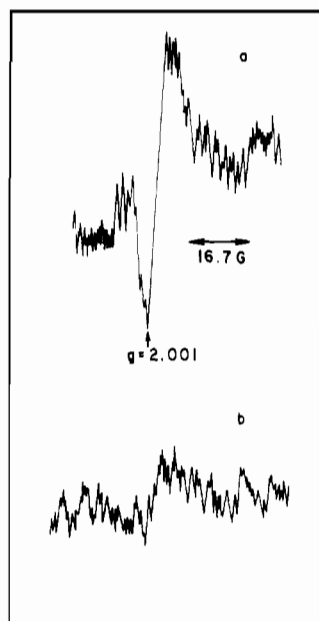


**Figure 8.** Spectra of intermediates generated in flash irradiations,  $\lambda_{\text{excit}} \geq 280$  nm, of Rh(ph)-(CH<sub>3</sub>OH)Br under various conditions: dotted line, solutions in deaerated acetonitrile; solid lines, solutions in deaerated 2-propanol-acetonitrile mixtures with [2-propanol]  $\geq 1.0$  M. Excitations were at  $\lambda_{\text{excit}} \geq 280$  nm with 250 J/pulse. Spectra were determined at the reaction time indicated in the figure.

In addition to the scavenging of CH<sub>2</sub>CN<sup>•</sup> radicals by 2-propanol, the oxidized rhodium(III) ligand radical can also be scavenged. However, the concentrations required for this scavenging are smaller than those used for scavenging CH<sub>2</sub>CN<sup>•</sup>, namely, [2-propanol]  $\leq 5.0 \times 10^{-1}$  M. The complexity of the optical transformations and the reduced size of the signals preclude the obtaining of an accurate value of the rate constant. However, an upper limit  $k \approx 2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  can be derived from these experiments.

The presence of halides in solutions of the rhodium(III) phthalocyanines, namely, solutions of Rh(ph)-(CH<sub>3</sub>OH)X in CH<sub>3</sub>CN containing appropriate concentrations of X with X = Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>, failed to reveal the photogeneration of halide radicals, e.g., Cl<sub>2</sub><sup>•-</sup>, Br<sub>2</sub><sup>•-</sup>, or I<sub>2</sub><sup>•-</sup>. In this regard, the transient behavior of the three members of the series Rh(ph)-(CH<sub>3</sub>OH)Cl, Rh(ph)-(CH<sub>3</sub>OH)Br, and Rh(ph)-(CH<sub>3</sub>OH)I, presented the same qualitative features in flash photolysis.

**ESR Measurements.** Although the rhodium(III) phthalocyanines are mute to the ESR, intense signals were recorded in steady-state irradiations,  $\lambda_{\text{excit}} \geq 320$  nm, in deaerated acetonitrile (Figure 9). The ESR spectra, obtained in photolyses of the acido(phthalocyanine)rhodium(III) complexes, have  $g \approx 2.001$  and exhibited small differences between them



**Figure 9.** ESR spectra obtained in steady-state irradiations,  $\lambda_{\text{excit}} \geq 320$  nm, of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$  (see also Table IV). Spectra were obtained in (a) deaerated 100%  $\text{CH}_3\text{CN}$  and (b) deaerated 1.0 M 2-propanol in  $\text{CH}_3\text{CN}$ .

**Table IV.** Parameters of the ESR Spectra Obtained in Steady-State Photolysis of Rhodium(III) Phthalocyanines

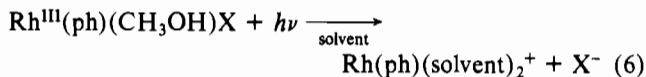
complex irradiated <sup>a</sup>	<i>g</i>	line width, G
$\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Cl}$	2.0037	6.60
$\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Br}$	2.0010	9.36
$\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{I}$	2.0042	10.75

<sup>a</sup> Solutions of the complexes in deaerated acetonitrile were irradiated at  $\lambda_{\text{excit}} \geq 320$  nm.

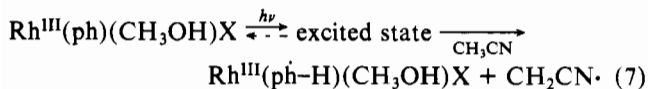
(Table IV). Such spectra were associated with the oxidized rhodium(III) ligand radicals. Indeed, 1.0 M 2-propanol eliminates more than 90% of the signal as is expected from our results in laser and flash photolysis. Other species, namely,  $\text{CH}_2\text{CN}\cdot$ , can be ignored on the basis that their steady-state concentrations are expected to be too small for detection in these experiments. Moreover, similar ESR spectra have been reported for the products obtained in redox reactions of metal phthalocyanines.

### Discussion

The results described above show that rhodium(III) phthalocyanines,  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{X}$  with  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , undergo a photolabilization process described in eq 6. The



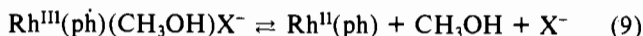
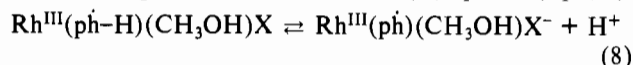
intermediates detected by various techniques signal that such a photolabilization is mediated by species that are generated in redox processes. Moreover, the evidence obtained in continuous-wave and flash photolysis indicate that halide radicals, namely,  $\text{X}\cdot$  or  $\text{X}_2\cdot$  with  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ , are not formed in the primary photochemical processes. The spectral transformations that were observed in a nanosecond time scale (Figure 5) were related to transients generated in a primary photooxidation of the acetonitrile (eq 7). Such a photo-



oxidation of the solvent can be described as a hydrogen abstraction by excited rhodium(III) phthalocyanine. This

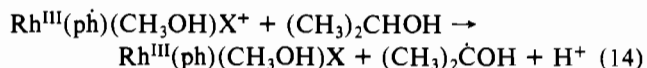
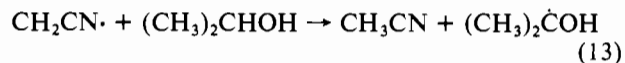
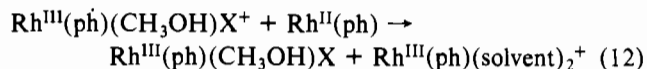
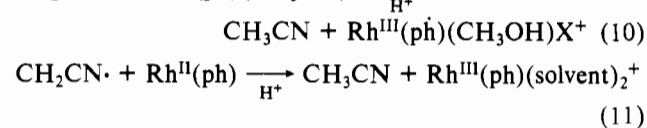
photoprocess is similar to the previously reported abstraction of hydrogen from appropriate donors by excited states of cobalt(II) and copper(II) phthalocyanines (eq 3).<sup>9,10</sup>

The spectral transformations observed in a nanosecond time scale show that the primary generated rhodium(III) ligand radical,  $\text{Rh}(\text{ph}-\text{H})(\text{CH}_3\text{OH})\text{X}$ , transforms into a species that has been assigned as a labile rhodium(II) species (eq 8, 9).



Such a formation of transient rhodium(II) is in agreement with the observed overall photolabilization process (eq 6). Namely, the formation of a labile rhodium(II) species in the early stages of the reaction will assist the substitution of the axially coordinated ligands from the originally inert rhodium(III).<sup>40</sup> The dependence of the half-lifetime of the overall transient transformation on the ionic strength (Table III) can be interpreted in terms of a complex process (eq 8) that precedes the transfer of the electron from the ligand radical to the metal (eq 9). It is interesting that similar intramolecular electron-transfer processes with millisecond lifetimes have been observed with several first-row transition-metal phthalocyanines.<sup>10,41</sup> The large rate,  $k \approx 1.4 \times 10^7 \text{ s}^{-1}$ , of the rhodium(III) complex can be explained in terms of an energy barrier for the intramolecular electron transfer smaller than those exhibited by first-row transition-metal phthalocyanines. Such a reduction in the barrier size can be partly associated with small contributions from Franck-Condon factors due to a convenient fit of the Rh(III) and Rh(II) centers in the phthalocyanine ring. Also, a mixing of the rhodium(III) and phthalocyanine electronic densities larger than that in the case of the first-row transition-metal complexes might contribute to make the electron-transfer reaction more favorable.<sup>42</sup>

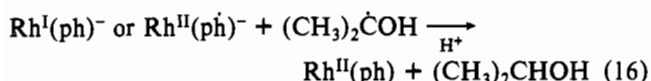
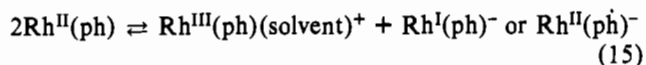
The reoxidation of the solvated rhodium(II) complex forms the product of the photolabilization process that is described in eq 6, namely,  $\text{Rh}^{\text{III}}(\text{ph})(\text{solvent})_2^+$ . The possible oxidants are the acetonitrile radical and/or the oxidized rhodium(III) ligand radical (eq 10–12). However, the large reactivity of  $\text{CH}_2\text{CN}\cdot$  with  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{X}$ , i.e.,  $k \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (see eq 10), suggests that its reaction with rhodium(II) phthalocyanine (eq 11) plays a small role under the experimental conditions used in this work. The reactivity of the radicals with 2-propanol (see Figure 8 and Table III) is described in eq 13 and 14. Moreover it is feasible that the fate of the



Rh(II) species is partly determined by eq 8 and 9 and reaction of the one-electron reduced species with 2-hydroxypropyl radicals, e.g., eq 15 and 16.

(40) J. Lilie, M. G. Simic, and J. F. Endicott, *Inorg. Chem.*, **14**, 2129 (1975).  
(41) G. Ferraudi and L. K. Patterson, *J. Chem. Soc., Dalton Trans.*, 476 (1980).

(42) A large mixing of metal orbitals with phthalocyanine orbitals is expected to stabilize the  $d_{z^2}$  orbital<sup>6</sup> and therefore reduce the endoergonicity of the Rh(III)/Rh(II) couple.



These observations on the photochemistry of rhodium(III) phthalocyanines show that the primary photoprocesses cannot be described as originating in excited states with acido to metal charge-transfer character. Such a primary photoreactivity can be assigned to reactive  $n\pi^*$  states similar to the excited state populated in ultraviolet irradiations of the monomeric copper(II) and cobalt(II) sulfophthalocyanines.<sup>9,10</sup> Another possibility is the induced oxidation of the solvent when acido to rhodium(III) states are populated. Photoprocesses with this nature, namely, the induced oxidation of the solvent by repolarization of the solvation sphere, have been previously reported for excitations of the acidopentaamminecobalt(III) complexes for acido to cobalt(III) charge-transfer states.<sup>25,43</sup>

The fact that the photochemistry of the rhodium(III) phthalocyanines is detected at low photonic energies, e.g.,  $\lambda_{\text{excit}} \approx 400 \text{ nm}$ ,<sup>44</sup> is inconsistent with an oxidation of the solvent by repolarization of the solvation sphere. In addition, the charge-transfer states that involve the phthalocyanine ligand, e.g.,  $\text{CTTM}_{\text{ph} \rightarrow \text{Rh}}$  and  $\text{CTTL}_{\text{Rh} \rightarrow \text{ph}}$ , are not expected to be able to oxidize the solvent by such a mechanism.

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**Registry No.** Rh(ph)(H<sub>2</sub>O)<sub>2</sub>HSO<sub>4</sub>, 81725-24-8; Rh(ph)-(CH<sub>3</sub>OH)Cl, 81725-25-9; Rh(ph)(CH<sub>3</sub>OH)Br, 81725-26-0; Rh(ph)(CH<sub>3</sub>OH)I, 81725-27-1.

(43) G. Ferraudi, J. F. Endicott, and J. Barber, *Inorg. Chem.*, **14**, 6406 (1975).

(44) S. Muralidharan and G. Ferraudi, work in progress.

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University of Notre Dame, Notre Dame, Indiana 46556

## Photochemistry of Transition-Metal Phthalocyanines. Monophotonic and Sequential Biphotonic Photochemical Processes of Copper(II) Tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in Nonaqueous Media

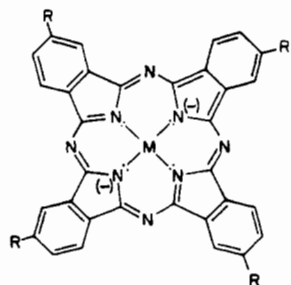
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The photochemistry of dimeric and monomeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in chloroform has been investigated by steady-state, flash and laser flash photolysis. The decay of a low-lying  $\pi\pi^*$  triplet-doublet with  $k \approx 2 \times 10^7 \text{ s}^{-1}$  was observed in laser flash photolysis. Similar observations were carried out with related complexes. Moreover, long-lived transformations were assigned to the formation of a copper(III) phthalocyanine. Product yields were determined as a function of the excitation wavelength and light intensity. Excitations on the Q band,  $\lambda \approx 600 \text{ nm}$ , with high intensities from a focused dye laser induce a photochemistry otherwise observed for excitations at  $\lambda \leq 350 \text{ nm}$ . Mechanisms involving short-lived  $n\pi^*$  states and two-photon photochemistry involving a low-lying and long-lived  $\pi\pi^*$  triplet-doublet are discussed.

### Introduction

The photochemistry of copper(II) tetrasulfophthalocyanine,  $\text{Cu}(\text{pts})^{2-}$  (I), has been recently investigated in aqueous so-

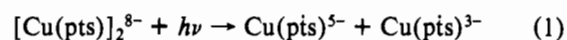


(I) R = SO<sub>3</sub>H

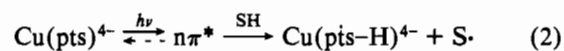
(II) R = SO<sub>2</sub>NH-C<sub>18</sub>H<sub>37</sub>

(III) R = H

lutions.<sup>1,2</sup> Ultraviolet irradiations of the dimeric species induce its photodissociation in copper(II) ligand radicals (eq 1). Such



a process was attributed to the population of either  $n\pi^*$  excited states or to charge-transfer states, which induce a transfer of charge between units of the dimer.<sup>1</sup> The photochemical properties of the monomeric species lend some support to the possibility of a reactive  $n\pi^*$  state. Indeed, the ultraviolet excitation of the monomeric species induces a hydrogen abstraction from appropriate hydrogen donors (eq 2). The



formation of Cu(II) ligand radicals in processes 1 and 2 suggests that the copper(I) and copper(III) complexes are unstable species with respect to the corresponding copper(II) ligand radicals. The photochemical generation of metastable copper(I) and copper(III) complexes has been recently observed in the ultraviolet photolyses of copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine,  $\text{Cu}(\text{pts-R})$  (II), in chloroform.<sup>3</sup> Although the copper(I) and copper(III) complexes do not transform into the copper(II) ligand radicals, such conversions have been observed with other metastable species. Indeed, one-electron-oxidized cobalt(II) and one-electron-reduced cobalt(III) ligand radicals undergo stabilizing intra-

(1) G. Ferraudi and E. V. Srisankar, *Inorg. Chem.*, **17**, 3164 (1978).

(2) G. Ferraudi, *Inorg. Chem.*, **18**, 1005 (1979).

(3) D. R. Prasad and G. Ferraudi, *Inorg. Chim. Acta*, **54**, L231 (1981).