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Contribution from the Radiation Laboratory,
University of Notre Dame, Notre Dame, Indiana 46556

Photochemistry of Transition-Metal Phthalocyanines. Photoredox-Induced Ligand Substitution in (Phthalocyanine)bis(pyridine)ruthenium(II)

D. RAJENDRA PRASAD and G. FERRAUDI*

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The photochemical properties of (phthalocyanine)bis(pyridine)ruthenium(II) have been investigated by flash photolysis, laser flash donors, and $n\pi^*$ photolysis. The observed photoprocesses, namely, the photoinduced decomposition of the complex and the photosubstitution of the pyridine ligand, are mediated by the same reduced ruthenium(II) ligand radical. Such a radical is formed in the abstraction of hydrogen, from given hydrogen donors, by $n\pi^*$ excited states of the phthalocyanine complex. Relaxation of excited states, populated by excitation at 300 nm, produces a low-lying $\pi\pi^*$ excited state with $t_{1/2} \approx 160$ ns. Such states can also be populated by 640-nm excitations. A mechanism for the photochemical transformations of $\mathrm{Ru(pc)(py)_2}$ is proposed.

Introduction

The ultraviolet photochemistry of the transition-metal phthalocyanines has recently received some attention.[1-6] Most of the investigated complexes undergo photoredox transformations when they are irradiated into the ultraviolet bands. Such transformations involve the abstraction of hydrogen from the solvent by excited states, e.g., $n\pi^*$ states of the phthalocyanine ligand (eq 1).[2-5] Also the ultraviolet irradiation of dimeric phthalocyanines induces the photoredox dissociation of dimers. The products of the photodissociation are either reduced and oxidized ligand radicals (eq 2) or species with an oxidized and reduced metal center (eq 3). The photochemical reactivity of the dimers can be attributed to either charge-transfer states, involving both units of the dimer, or to oxidizing $n\pi^*$ states.

$$\mathrm{M^{II}(pc)} \overset{h\nu}{\rightleftarrows} n\pi^* \xrightarrow{\text{solvent}} \mathrm{M^{II}(\dot{p}cH)} \qquad (1)$$
$$(\mathrm{M^{II}} = \mathrm{Co^{II}, Cu^{II}})$$

$$\mathrm{[M^{II}(pc)]_2} \overset{h\nu}{\rightleftarrows} \text{excited state} \rightarrow \mathrm{M^{II}(\dot{p}c)^-} + \mathrm{M^{II}(\dot{p}c)^+} \qquad (2)$$
$$(\mathrm{M^{II}} = \mathrm{Cu^{II}})$$

$$\mathrm{[M^{II}(pc)]_2} \overset{h\nu}{\rightleftarrows} \text{excited state} \rightarrow \mathrm{M^{I}(pc)^-} + \mathrm{M^{III}(pc)^+} \qquad (3)$$
$$(\mathrm{M^{II}} = \mathrm{Co^{II}})$$

Some phthalocyanines have been observed to undergo a photoinduced electron transfer to a given acceptor, O in eq 4, when they are excited at wavelengths of the Q band in the near-infrared region.[6,7] This behavior has been equated in some cases to the reactivity of low-lying charge-transfer states, CT, that involve the electronic density of the phthalocyanine ligand and to ligand-centered $\pi\pi^*$ states.[6]

$$\mathrm{M^{II}(pc)} \overset{h\nu}{\rightleftarrows} \mathrm{CT} \xrightarrow{\mathrm{O}} (\text{products of } \mathrm{M^{II}(pc)} \text{ oxidation}) + \mathrm{O^{-}\cdot} \qquad (4)$$

The photochemical behavior of the ruthenium(II) phthalocyanines was investigated by James et al.[8,9] The photochemistry of these compounds is largely dependent on the solvent, and for a given solvent, it depends on the presence of potential ligands, e.g., CO. Two different photoreactions, namely, the photosubstitution of the axial ligand and phthalocyanine decomposition, have been reported. We have investigated in this work the intermediates of these reactions in order to correlate the photochemical behavior of the ruthenium(II) phthalocyanines with those reported for other transition-metal phthalocyanines and/or other ruthenium(II) complexes.

Experimental Section

Photochemical Procedures. Continuous photolyses were carried out in a Rayonet Minireactor fitted with an appropriate lamp for irradiations at 300 nm. Streams of Ar were used for the deaeration of the solutions. Moreover, the homogeneity of the reaction medium was preserved during the irradiation by stirring the liquid with a magnetic stirrer. Quantum yields were obtained from the slopes of concentration vs. irradiation time graphics. The light intensity was periodically determined with tris(oxalato)ferrate(III).[10]

The apparatus used for flash photolysis was described elsewhere.[11] Two xenon flash lamps, Xenon Corp. FP8-100C, were simultaneously fired at energies between 250 and 40 J/pulse. The flash duration limits the time resolution of this apparatus to observation times longer than 50 μs. The laser flash photolysis unit used for observations at times shorter than 30 μs is a modification of one previously described.[12] Flash irradiations can now be performed either with a Molectron 400 nitrogen laser, for excitations at 337 nm, or with a Quanta Ray neodymium yag pumped dye laser, for excitations at 640 nm with a DCM dye. The rest of the apparatus, namely, the detection and data processing systems, remains the same. Solutions of the photolyte were refreshed after each flash irradiation in either flash or laser flash experiments.

Analytical Procedures. Chloride ions were analyzed by extraction from the organic solvents with distilled water. Their concentration was determined with a HNU specific-ion electrode. Calibration curves were constructed under the same experimental conditions used in the photochemical experiments.

A procedure similar to the one described for the analysis of chloride ions was used for pyridine. The concentration of pyridine in the aqueous phase was determined by means of the 255-nm absorbance. Solutions of $\mathrm{Ru(pc)(py)_2}$ maintained in the dark but treated otherwise as the irradiated samples were used in the preparation of blanks.

Materials. $\mathrm{Ru(pc)(py)_2}$ and $\mathrm{Ru(pc)(py)CO}$ were prepared and purified according to reported procedures.[8,9]

The solvents used for photochemical experiments, Aldrich Gold Label acetonitrile, dichloromethane, and benzene, were distilled in an all-glass distillation apparatus fitted with a 40-theoretical-plate fraction column.

Results

Transient Behavior. The transients generated in flash photolysis of $\mathrm{Ru(pc)(py)_2}$, $\lambda_{\mathrm{excit}} \geq 320$ nm, were investigated in various solvents, namely, acetonitrile, dichloromethane, and

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(1) Ligand abbreviations: pc, phthalocyanine; py, pyridine.
(2) G. Ferraudi and E. V. Srisankar, *Inorg. Chem.*, **17**, 3164 (1978).
(3) G. Ferraudi, *Inorg. Chem.*, **18**, 1005 (1979).
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(5) D. R. Prasad and G. Ferraudi, *Inorg. Chem.*, **21**, 2967 (1982).
(6) A. B. P. Lever, S. Licoccia, B. S. Ramaswamy, S. A. Kandil, and D. V. Stynes, *Inorg. Chim. Acta*, **51**, 169 (1981).
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(12) R. D. Small and J. Scaiano, *J. Phys. Chem.*, **81**, 828 (1977).

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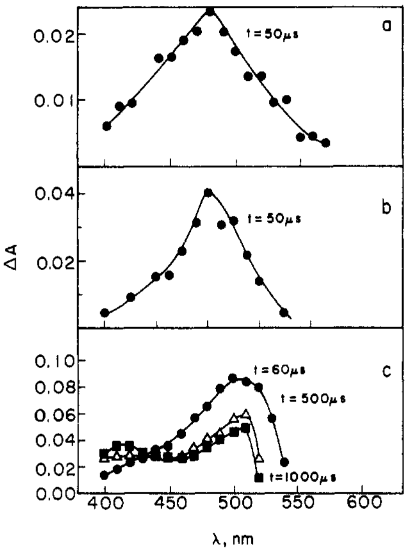

Figure 1. Transient spectra obtained in flash photolysis of $Ru(pc)(py)_2$ in various solvents: (a) acetonitrile; (b) benzene; (c) dichloromethane. Excitations were carried out with 250 J/pulse flashes at $\lambda_{excit} \geq 320$ nm of deaerated solutions.

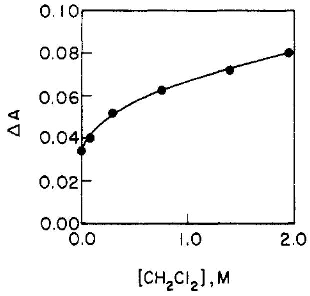

Figure 2. Dependence of the yield of the ruthenium(II) ligand radical on dichloromethane concentration. Flash irradiations, $\lambda_{excit} \geq 320$ nm, were performed on $Ru(pc)(py)_2$ in deaerated benzene–dichloromethane mixtures with 250 J/pulse flashes.

Table I. Rate Constants for the Disappearance of the Ruthenium(II) Ligand Radical

solvent[b]	$t_{1/2}$,[a] μs	k, s^{-1}
benzene	78 ± 9	7.6×10^3
dichloromethane	50 ± 7	1.2×10^4
acetonitrile	25 ± 9	2.3×10^4

[a] Average value obtained for irradiation with various flash intensities, e.g., pulses with energies between 250 and 40 J/pulse. [b] Deaerated solutions of $Ru(pc)(py)_2$ irradiated at $\lambda_{excit} \geqslant 320$ nm.

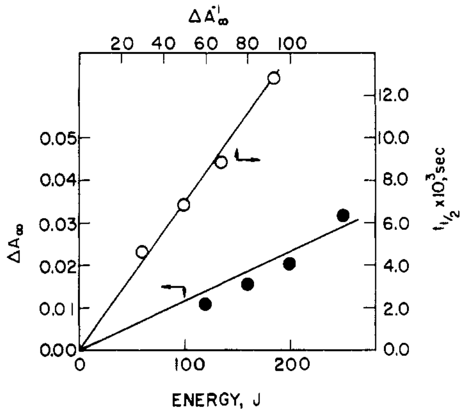

Figure 3. Dependence of the absorbance at an infinite reaction time, ΔA_∞, and half-life, $t_{1/2}$, on flash energy for the absorbance growth observed at 420 nm (see Figure 1). Irradiations of $Ru(pc)(py)_2$ were in deaerated CH_2Cl_2.

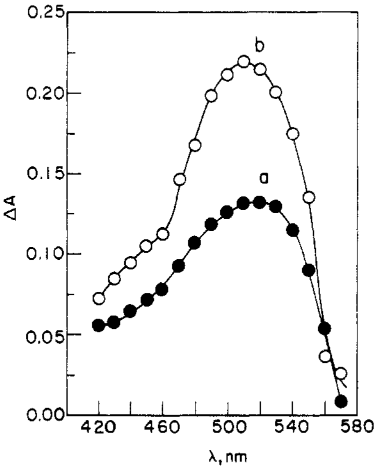

Figure 4. Transient spectra determined in 337-nm laser flash irradiations of $Ru(pc)(py)_2$ in (a) deaerated benzene and (b) deaerated dichloromethane.

benzene. Ultraviolet irradiations of $Ru(pc)(py)_2$ in these solvents produce the same transient spectra at short reaction times, e.g., $t \approx 100$ μs (Figure 1). Such spectra exhibited maxima at $\lambda_{max} \approx 500$ nm in agreement with those reported for one-electron-reduced ligand radical species.[2,3,13] The yield of this ruthenium(II) ligand radical depends on the solvent; namely, the smallest value of the yield was obtained in benzene while the largest was determined for irradiations of the complex in dichloromethane (Figure 2). Such a behavior was attributed to a competition between benzene and dichloromethane for a precursor, namely, an $n\pi^*$ excited state. A ratio of the rate constants, $k_{benzene}/k_{dichloromethane} = 0.4$, was obtained from the dependence of the ligand radical yield on dichloromethane concentration. Moreover, the rate of the ruthenium(II) ligand radical disappearance shows a first-order dependence on transient concentration and the rate constant for such a process reflects a moderate influence from the solvent (Table I). In addition, the decay of the 500-nm absorbance is followed by a growth of the optical density at 420 nm, namely, a growth that is observed at longer times than those required for more than 70% disappearance of the 500-nm absorbance (Figure 1). Such a growth is a process with a second-order rate law as is indicated by the dependence of the reaction half-life on flash energy (Figure 3). A ratio of the second-order rate constant to the extinction coefficient, $k/\epsilon = (1.5 \pm 0.3) \times 10^5$ cm s^{-1}, was obtained at 420 nm.

Flash irradiations of $Ru(pc)(py)_2$ in CO-saturated benzene or CO-saturated dichloromethane reveal the formation of $Ru(pc)(py)CO$ on a millisecond time scale. The rate of formation exhibited a second-order dependence on flash energy. Moreover, the rate constant for the decay of the ruthenium(II) ligand radical in solutions with CO shows no difference from the one measured for the same species in Ar-saturated solutions.

Excitation of $Ru(pc)(py)_2$ in deaerated solutions at $\lambda_{excit} \geq 550$ nm failed to produce spectral transformations above the detection limit of the flash photolysis unit, namely, an absorbance change $\Delta A \leq \pm 1 \times 10^{-3}$ for a 20-cm optical path and reaction times $t \geq 50$ μs.

The precursors of the transients observed in a microsecond–millisecond time scale were also investigated in a nanosecond time scale by laser flash photolysis. A transient spectrum with $\lambda_{max} \approx 500$ nm was observed in 337-nm laser

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(13) L. D. Rollman and R. T. Iwamoto, *J. Am. Chem. Soc.*, **90**, 1455 (1968).

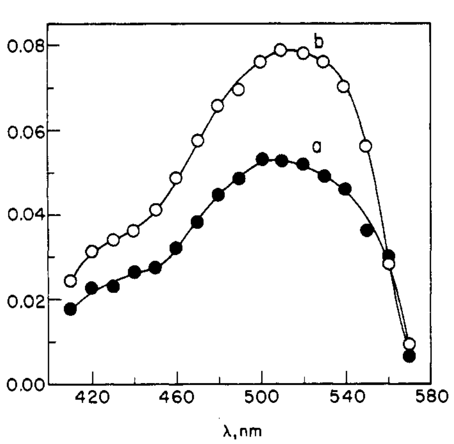

Figure 5. Spectra of the $^3\pi\pi^*$ state obtained in 640-nm laser flash irradiations of $Ru(pc)(py)_2$ in (a) deaerated benzene and (b) deaerated dichloromethane.

Table II. Product Yields for 300-nm Photolysis of $Ru(pc)(py)_2$

conditions[a]	$10^2\phi(py)$	$10^2\phi(Cl^-)$	$10^3\phi(Ru(pc)(py)X)$
CO-saturated benzene	1.4 ± 0.2		6.6 ± 0.3[b]
dichloromethane	5.5 ± 0.3	1.5 ± 0.2	
CO-saturated dichloromethane	5.5 ± 0.2	1.4 ± 0.2	5.3 ± 0.4[b]
O_2-saturated dichloromethane	5.8 ± 0.4	4.1 ± 0.2	
acetonitrile			4.8 ± 0.5[c]

[a] Deaerated with Ar unless stated; $I_0 = 1.1 \times 10^{-4}$ einstein/(L min). [b] X = CO. [c] $X = CH_3CN$.

flash irradiations of $Ru(pc)(py)_2$ in deaerated benzene (Figure 4). Such spectra disappear with a rate that exhibits a first-order dependence on transient concentration. A rate constant, $k = 3.5 \times 10^6$ s^{-1}, was determined for such a process. It is possible to attribute these spectral transformations to the relaxation of a low-lying $\pi\pi^*$ excited state (see below). The ruthenium(II) ligand radical was also observed in 337-nm laser flash irradiations of $Ru(pc)(py)_2$ in benzene–dichloromethane mixtures. Such observations were carried out at reaction times comparable to those used in our conventional flash photolysis experiments, namely, in a microsecond time scale (see above). These experiments show that, although the yield of the ruthenium(II) ligand radical increases with dichloromethane concentration in a manner already described above, the lifetime of the $\pi\pi^*$ excited state is independent of the solvent composition. A rate constant, $k \simeq 3.7 \times 10^6$ s^{-1}, was obtained from measurements at various concentrations of dichloromethane, namely, $[CH_2Cl_2] \leq 1.5$ M.

Laser irradiations of $Ru(pc)(py)_2$ at wavelengths of the Q band, $\lambda_{excit} \approx 640$ nm, produce a transient spectra with $\lambda_{max} \approx 500$ nm (Figure 5). The same spectrum was recorded in deaerated benzene or dichloromethane, and it was attributed to the same $\pi\pi^*$ excited state that was reported above. Rate constants $k = 4.9 \times 10^6$ s^{-1} in benzene and $k = 4.2 \times 10^6$ s^{-1} in dichloromethane were determined for the first-order disappearance of the transient spectra. Such a disappearance, followed on a microsecond time scale, does not leave the characteristic spectrum of the ruthenium(II) ligand radical that is observed for 337-nm laser flash photolysis (see above and Figure 5).

Continuous Photolysis. The 300-nm irradiation of $Ru(pc)(py)_2$ in deaerated CH_2Cl_2 produces the decomposition of the complex. In this regard our results agree with those reported by James et al.[8,9] The opening of the macrocycle is indicated by a decrease of the absorbance at wavelengths where the complex exhibits characteristic ligand absorptions (Figure 6). We found that the photodecomposition of the complex induces the liberation of pyridine and chloride ions (Table II).

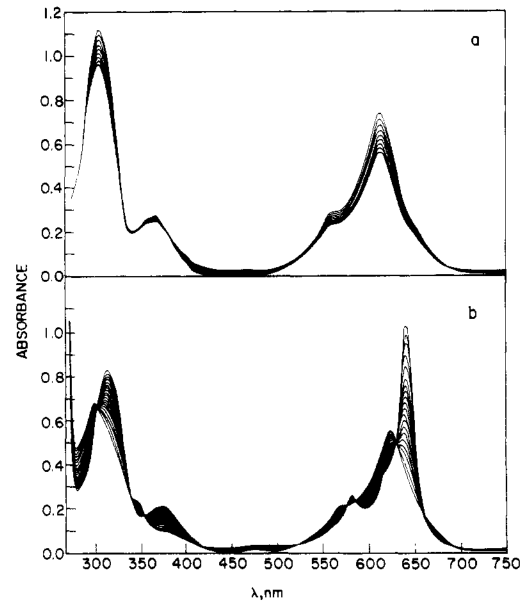

Figure 6. Spectral transformations recorded in 300-nm continuous photolysis of $Ru(pc)(py)_2$ in (a) deaerated dichloromethane and (b) CO-saturated benzene.

The yields of pyridine and chloride ions determined in solutions saturated under 1 atm of CO were the same obtained with Ar-saturated solutions (Table II). Moreover, only a minor fraction of the photochemical transformation results in the formation of the monocarbonyl complex in CO-saturated solutions (Table II).

The 300-nm irradiation of $Ru(pc)(py)_2$, $I_0 = 1.1 \times 10^{-4}$ einstein/(L min), in deaerated benzene produces small spectral transformations. Such transformations ceased for irradiations longer than 5 s. However, photolyses of $Ru(pc)(py)_2$ in the presence of CO induce the formation of the monocarbonyl complex (Figure 6). The concentration of the photosubstitution product increases linearly with irradiation time.

Discussion

It has been demonstrated in this and James' work that the photochemical transformations of $Ru(pc)(py)_2$ are largely dependent on the solvent.[8,9] Indeed the overall photochemical transformation can be described as either a photosubstitution of the axial ligand, e.g., in CO-saturated benzene or acetonitrile, or the photodecomposition of the phthalocyanine, e.g., in dichloromethane. Our observations in flash photolysis indicate that these two processes are mediated by a ruthenium(II) ligand radical with $\lambda_{max} \approx 500$ nm and microsecond lifetimes. Therefore the dependence of the photochemistry of $Ru(pc)(py)_2$ on the solvent can be associated with changes of the reactivity of given intermediates and the ability of the solvent to donate hydrogen. In this regard the primary process can be described as a hydrogen abstraction from the solvent, namely, by $n\pi^*$ states of the phthalocyanine ligand. Similar processes have been observed with other phthalocyanines, e.g., the phthalocyanines of cobalt(II) and copper(II).[2,4,5] The laser flash photolysis experiments in benzene–dichloromethane mixtures reveal the formation of two species on a nanosecond time scale. One of them has been assigned as a relatively long-lived $\pi\pi^*$ excited state, e.g., $a_{1u}(\pi) \rightarrow e_g(\pi^*)$, and the other species as the ruthenium(II) ligand radical described above. The validity of the assignment of one of the transients as $^3\pi\pi^*$ is based on the spectrum reported for this state, e.g.: in photolyses of several phthalocyanines with close-shell metal ions.[14-16] Such a long-lived excited state must also be the $\pi\pi^*$

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(14) J. R. Darwent, I. M. Cubbin, and D. Phillips, *J. Chem. Soc., Faraday Trans. 2*, **78**, 347 (1982).

luminescent state.[19] In addition, our observations show that such a state is populated in a time shorter than the resolution of our laser flash photolysis apparatus for excitations at $\lambda_{\text{excit}} \approx 337$ nm. This behavior suggests that, as in the case of the copper(II) phthalocyanines, the low-lying state is populated by relaxation of states placed above this state, namely, the $\pi\pi^*$ state originated in $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ and/or $n\pi^*$.[5,19] In this regard our observations on the photochemistry of $Ru(pc)(py)_2$ are in good agreement with predictions based on theoretical calculations of Gouterman and spectroscopic observations of Huang et al.[19,20] The spectrum of the other species, namely, the ruthenium(II) ligand radical, is similar to those of ligand radicals generated in photochemical and electrochemical reaction of various phthalocyanines.[2,3,9,21] Indeed, the spectrum of the oxidized ruthenium(II) phthalocyanine ligand radical is the same spectrum obtained in one-electron oxidations of other phthalocyanines.[2,3,21] Therefore one can expect minor differences between the spectrum of the reduced ruthenium(II) ligand radical and those reported for other reduced phthalocyanine ligand radicals.[2,3,9,21]

The increases of the yield of ruthenium(II) ligand radical with dichloromethane concentration (Figure 2) suggest a competition between dichloromethane and benzene for the reactive $n\pi^*$ excited state. Measurements in flash photolysis gave the ratio of the rate constants for the reactions of the $n\pi^*$ state with benzene and dichloromethane $k_{\text{benzene}}/k_{\text{dichloromethane}} = 0.4$, which is in agreement with the differences in the ability for hydrogen donation of the two solvents. A mechanism that explains our observations in the photolyses of the ruthenium(II) phthalocyanine in dichloromethane is described in eq 5–11.

$$\mathrm{Ru^{II}(pc)(py)_2} \underset{}{\overset{h\nu}{\rightleftarrows}} n\pi^* \xrightarrow[k_1]{\mathrm{CH_2Cl_2}} \mathrm{Ru^{II}(\dot{p}cH)(py)_2} + \mathrm{CHCl_2}\cdot \tag{5}$$

$$\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Ru^{I}(pc)(py)_2^-} + \mathrm{H^+} \tag{6}$$

$$\mathrm{Ru^{I}(pc)(py)_2^-} + \mathrm{CH_2Cl_2} \xrightarrow[k_3]{} \mathrm{Ru(pc)(py)CH_2Cl} + \mathrm{Cl^-} + \mathrm{py} \tag{7}$$

$$\mathrm{Ru(pc)(py)CH_2Cl} \xrightarrow[k_4 >> k_3]{} \mathrm{py} + \text{phthalimide} + \text{other products} \tag{8}$$

$$\mathrm{Ru^{I}(pc)(py)_2^-} + \mathrm{CHCl_2}\cdot \xrightarrow[k_5]{} \mathrm{Ru^{II}(pc)(py)CHCl_2} + \mathrm{py} \tag{9}$$

$$\mathrm{CHCl_2}\cdot + \mathrm{CHCl_2}\cdot \xrightarrow[k_6]{} \mathrm{C_2H_2Cl_4} \tag{10}$$

$$\mathrm{Ru^{II}(pc)(py)CHCl_2} + \mathrm{L} \xrightarrow[k_7]{\mathrm{H^+}} \mathrm{Ru^{II}(pc)(py)L} + \mathrm{CH_2Cl_2} \tag{11}$$

(L = CO, py, other ligands)

The equilibration of the ligand radical with a ruthenium(I) species (eq 6) is proposed in order to explain the photoinduced lability that allows the exchange of pyridine by other potential ligands in the time scale of our experiments. Examples of the intramolecular electron-transfer process, namely, charge transfer from ligand to metal and metal to ligand in ligand radical species, have been reported for various phthalocyanines and porphyrins.[3,22,23]

The mechanism described above attributes the formation of chloride ions to an attack of the chlorinated solvent by ruthenium(I) (eq 7), while the formation of free pyridine is associated with the decomposition of a ruthenium–alkyl species (eq 8).[24] The ratio of the pyridine and chloride yields can be expressed in terms of the rate constants k_3 and k_5 (see Appendix). The values obtained for these rate constants demonstrate that reaction 7 can only make a significant contribution to the product formation in steady-state irradiations with low light intensities, e.g., $I_0 \leq 10^{-4}$ einstein/(L min). However, reaction 9 will make large contributions in flash and steady state irradiations.

The photochemistry of $Ru(pc)(py)_2$ in benzene or acetonitrile can be described by mechanisms similar to the one proposed for photolysis in CH_2Cl_2 if appropriate changes are introduced to the reaction scheme (eq 5–11). Indeed, two major changes are expected in non-chlorinated solvents, namely, that $CHCl_2\cdot$ will be replaced by the corresponding solvent radicals $C_6H_5\cdot$ and $CH_2CN\cdot$ and that the Ru(I) complex will not react with solvent molecules; e.g., reactions 7 and 8 can be eliminated from the mechanism.

It is possible at this point to compare the photochemical behavior described above for $Ru(pc)(py)_2$ with that of other related ruthenium(II) complexes. Indeed complexes with unsaturated ligands, e.g., *trans*-$Ru(NH_3)_4LL'^{2+}$, where L and L′ are various pyridine derivatives, undergo various photosubstitutions when they are irradiated in their visible and ultraviolet absorption bands.[25,26] Such a behavior clearly contrasts with that reported above for $Ru(pc)(py)_2$, and this disparity must be attributed to the population of different photoreactive states. It has been proposed that the photoreactivity of $Ru(NH_3)_4LL'^{2+}$ complexes results from a rapid internal conversion of directly populated metal to ligand charge-transfer states, MLCT, to the reactive lowest lying ligand field state, LF. The change of the four amino groups of $Ru(NH_3)_4LL'^{2+}$ by a phthalocyanine ligand in $Ru(pc)(py)_2$ must introduce strong perturbations in the electronic density of the metal center. However, one can expect that some of the LF states in $Ru(pc)(py)_2$ will remain at lower energies than the CTTL states. Therefore it seems feasible that the potentially reactive LF state achieves no population from the ligand-centered states, e.g., $\pi\pi^*$, produced in the initial ultraviolet excitation, or that it undergoes a rapid internal conversion to low-lying states.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2317 from the Notre Dame Radiation Laboratory. We are thankful to Dr. P. K. Das for his assistance in the laser flash experiments.

Appendix

The yields of chloride ions and pyridine can be expressed

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(15) A. Harriman, M. Richoux, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1175 (1981).

(16) Although there is some evidence that low-lying charge transfer states determine the lifetime of $^3\pi\pi^*$,[17,18] we found no spectroscopic evidence of their presence in time-resolved experiments.

(17) A. B. P. Lever, S. R. Pickens, P. C. Minor, S. Licoccia, B. S. Ramaswamy, and K. Magnell, *J. Am. Chem. Soc.*, **103**, 6800 (1981).

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(19) T. H. Huang, K. E. Rieckhoff, and E. Voight, *J. Phys. Chem.*, **85**, 3322 (1981).

(20) A. M. Schaffer, M. Gouterman, and E. R. Davidson, *Theor. Chim. Acta*, **30**, 9 (1973).

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(22) L. K. Patterson and G. Ferraudi, *J. Chem. Soc., Dalton Trans.*, 476 (1980).

(23) M. Barley, J. Y. Becker, G. Domazetis, D. Dolphin, and B. R. James, *J. Chem. Soc., Chem. Commun.*, 983 (1981).

(24) A similar reduction of the halogen–carbon bonds by cobalt(I) phthalocyanine has been previously reported by P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc. A*, 90 (1968), and ref 4 and 5.

(25) P. C. Ford, *Rev. Chem. Intermed.*, **2**, 267 (1979).

(26) E. Tfouni and P. C. Ford, *Inorg. Chem.*, **19**, 72 (1980).

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by eq 12 and 13. Therefore, the ratio of the chloride ion to

$$\phi_{py} = \frac{1}{I_0}\frac{\partial[\mathrm{py}]}{\partial t} = \frac{1}{I_0}(2k_3' + k_5[\mathrm{R}])[\mathrm{Ru^I}] \qquad (12)$$

$$\phi_{Cl^-} = \frac{1}{I_0}\frac{\partial[\mathrm{Cl^-}]}{\partial t} = \frac{1}{I_0}(k_3'[\mathrm{Ru^I}]) \qquad (13)$$

$(k_3' = k_3[\mathrm{CH_2Cl_2}]$, $[\mathrm{R}] = [\mathrm{CHCl_2\cdot}]$, and $[\mathrm{Ru^I}] = [\mathrm{Ru^I(pc)(py)_2^-}])$

pyridine yield is as shown by eq 14. The steady-state

$$\frac{\phi_{Cl^-}}{\phi_{py}} = \frac{k_3'}{2k_3' + k_5[\mathrm{R}]} \qquad (14)$$

treatment of R in the mechanism, eq 5–11, gives a steady-state concentration of R (eq 15) which depends on the yield, ϕ, the

$$[\mathrm{R\cdot}] \approx (\phi I_0)^{1/2}k_5^{-1/2} \approx (2 \times 10^{-3})k_5^{-1/2} \qquad (15)$$

absorbed light intensity, I_0, and the rate constant k_5. The substitution of eq 15 in eq 14 and the rearrangement of the resulting equation gives eq 16. Hence if reaction 5 is a

$$k_5^{1/2}/k_3' = 8.3 \times 10^2 \qquad (16)$$

diffusion-controlled reaction, e.g., $k_5 \approx 5 \times 10^9$ M^{-1} s^{-1}, then the value of $k_5/\epsilon = 1.5 \times 10^5$ cm s^{-1}, obtained in flash photolysis, gives an extinction, $\epsilon \approx 3 \times 10^4$ M^{-1} cm^{-1}, that is in good agreement with those reported for other one-electron-reduced ligand radicals.[13] Moreover, the rate constant for reaction 7 obtained under this approximation is $k_3' \approx 90$ s^{-1}.

Registry No. Ru(pc)(py)$_2$, 68588-46-9; Ru(pc)(py)CO, 67588-47-0; py, 110-86-1; Cl$^-$, 16887-00-6; CH$_2$Cl$_2$, 75-09-2; CO, 630-08-0; CH$_3$CN, 75-05-8; Ru(pc)(py)CH$_3$CN, 82665-23-4; benzene, 71-43-2.

Contribution from the Department of Chemistry,
York University, Downsview, Ontario, Canada M3J 1P3

Comparative Kinetics of Axial Ligation to Ruthenium and Iron Porphyrin and Phthalocyanine Complexes. Relationship between Spin State and Cis and Trans Effects

FRANK POMPOSO, DAVID CARRUTHERS, and DENNIS V. STYNES*

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Kinetic data for the dissociative axial substitution reactions of benzyl isocyanide (BzNC) and CO complexes of ruthenium octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), and phthalocyanine (Pc) complexes are reported and compared with corresponding data for iron complexes. The relative lability of BzNC complexes containing 1-methylimidazole (CH$_3$Im) and 4-*tert*-butylpyridine (*t*-Bupy) is RuPc < RuP << FePc < FeP. The porphyrin systems are inherently more labile by 3–5 kcal/mol in ΔG^*. In complexes with two weak-field axial ligands, a spin change occurring along the reaction coordinate for ligand dissociation is proposed to account for an additional ~3 kcal/mol lower ΔG^* only in the iron porphyrin systems. Trans effects of CO and BzNC are rationalized in terms of spin-state effects in the transition state.

Introduction

Extensive kinetic studies of iron(II) complexes of porphyrins[1–4] and phthalocyanines[5–7] have shown a substantially different lability in dissociative axial ligation of imidazoles, pyridines, carbon monoxide, and isocyanides. In carbonylruthenium porphyrins, RuP(CO)(L), a remarkable lability of nitrogen donors (L) trans to CO is reported.[8,9] A similar labilization is observed in isocyanide derivatives of ruthenium porphyrins.[10] However, the corresponding RuP(CH$_3$Im)$_2$ or RuP(py)$_2$ complexes are very inert.[11]

It has been proposed that spin-state changes and the consequent movement of the iron with respect to the tetradentate ligand plane may be involved in labilization effects in axial ligand substitution reactions in the iron complexes.[5] For hemes, high-spin pentacoordinate complexes can be isolated and studied. No report of pentacoordinate Fe(II) phthalocyanines has appeared although extensive kinetic evidence for pentacoordinate intermediates in the dissociative substitution reactions of six-coordinate FeN$_4$L$_2$ systems exists.[5–7] Discussion of the spin state of such intermediates in FePc complexes has been speculative.[5] A comparative study of the ruthenium complexes of porphyrins and phthalocyanines is of interest since the ruthenium is not expected to give high-spin complexes and the greater size of ruthenium, relative to iron, makes it somewhat too large for the phthalocyanine ring. Thus the ruthenium complexes might be expected to provide insight into spin-state and ring size effects, features given particular importance in hemes and hemoproteins.

Several reports of studies of ruthenium phthalocyanines have appeared during the course of our work.[12–14] Sweigart[15] has reported kinetic comparisons of axial ligand lability in FePc and RuPc complexes of phosphines and phosphites. Herein we describe comparisons of axial ligand lability in isocyanide and carbon monoxide complexes of RuP, RuPc, FeP, and FePc and reconcile enormous differences in axial ligand lability in terms of cis and trans effects.

Experimental Section

Crude RuPc and RuPc(CO) were prepared from phthalonitrile and RuCl$_3$ or Ru$_3$(CO)$_{12}$, respectively, by methods essentially the same as described elsewhere.[12,15] RuPc(CO)(L), L = CH$_3$Im and *t*-Bupy, compounds, were prepared as described by James.[12] RuTPP(C-

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