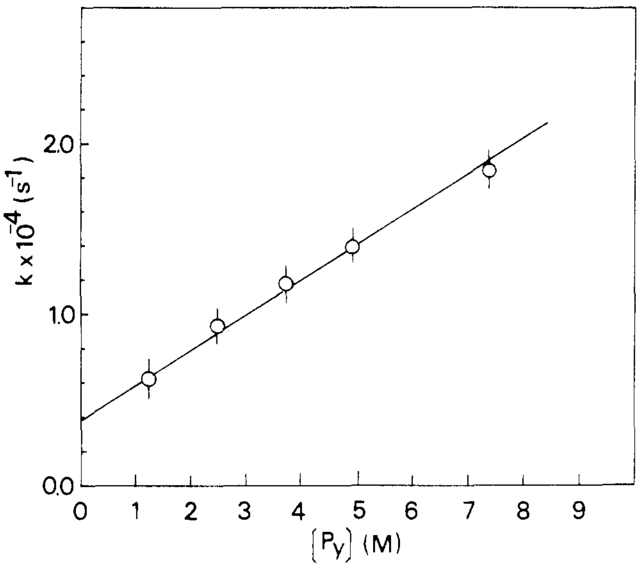

Figure 3. Plot of k vs. pyridine concentration, [py], obtained at 200 K.

photolysis studies mentioned above, the photochemical reactions of Ni^{II}TPP in the mixed solvent are represented as

$$\mathrm{Ni^{II}TPP(py) + py \underset{dark}{\overset{h\nu}{\rightleftharpoons}} Ni^{II}TPP(py)_2} \quad (T = 280.4\ \mathrm{K}) \qquad (2)$$

$$\mathrm{Ni^{II}TPP(py)_2 \underset{dark}{\overset{h\nu}{\rightleftharpoons}} Ni^{II}TPP(py) + py} \quad (T = 181.2\ \mathrm{K}) \qquad (3)$$

Therefore, the laser flash is considered to result in the shift of the equilibrium shown by reaction 1 owing to the photoinduced attachment of py to Ni^{II}TPP(py) as well as detachment of py from Ni^{II}TPP(py)$_2$. Accordingly, the decay process of the transient is interpreted in terms of the recovery of the equilibrium: the decay rate constant, k, is expressed as

$$k = k_f[\mathrm{py}] + k_b$$

Figure 3 shows the plot of k as a function of pyridine concentration, [py], at 200 K. From the slope and the intercept of the line, we obtain $k_f = 2.06 \times 10^4$ M^{-1} s^{-1}. The fact that k has a linear relation to [py] supports the conclusion that the photochemistry of the solution is expressed by reactions 2 and 3; i.e., the photoexcited Ni^{II}TPP(py)$_2$ releases a pyridine molecule, and the photoexcited Ni^{II}TPP(py) reacts with a pyridine molecule to form Ni^{II}TPP(py)$_2$. The previous results obtained by picosecond photolysis of Ni^{II}TPP in pyridine solutions were interpreted on the assumption that two pyridine molecules are concerned in the photochemistry of Ni^{II}TPP.[7,8] However, the present results show that only one pyridine molecule is responsible for the photochemistry of Ni^{II}TPP in a mixed solvent of pyridine and toluene.

From k obtained by laser photolysis and the equilibrium constant K calculated from the spectral changes, k_f and k_b can be determined at various temperatures. The usual Arrhenius expressions for k_f and k_b are given by

$$k_f = (6.5 \pm 0.5) \times 10^7 \exp[-(3230 \pm 300)/RT]\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_b = (2.1 \pm 0.2) \times 10^{14} \exp[-(9400 \pm 500)/RT]\ \mathrm{s^{-1}}$$

The fact that the preexponential factor in k_b exceeds 10^{13} suggests that the activation entropy for the dissociation of py from Ni^{II}TPP(py)$_2$ is necessarily a positive one.

The photochemistry of Ni^{II}TPP(py) and Ni^{II}TPP(py)$_2$ is considered to be closely related to the nature of their excited states. However, neither of the excited states of Ni^{II}TPP(py) and Ni^{II}TPP(py)$_2$ was observed in the present study because of their short lifetimes in comparison with the duration of the laser flash (20 ns). Straub and his co-workers[10] have carried out picosecond photolysis studies of nickel(II) protoporphyrin dimethyl ester and found two excited states having decay times of 10 and 250 ps. Picosecond photolysis studies of Ni^{II}TPP in a pyridine solution at room temperature indicate that (1) the metal excited singlet state, $^1A_{1g}$, of Ni^{II}TPP(py)$_2$ releases the ligands and (2) the metal excited triplet state, $^3B_{1g}$, of Ni^{II}TPP binds the ligands.[7,8] In the present study, we have reconfirmed, by using a conventional laser photolysis technique, that Ni^{II}TPP in a mixed solvent of pyridine and toluene undergoes photoinduced ligand attachment and detachment. From the measurements of the decay rate constants of the transients in the temperature range 300–180 K, the apparent activation energies and entropies for k_f and k_b were determined. These results are considered to be useful for further understanding of metalloporphyrin photochemistry as well as the association and dissociation processes of ligands in metalloporphyrins.

Registry No. Ni^{II}TPP, 14172-92-0; Ni^{II}TPP(py), 36046-97-6; Ni^{II}TPP(py)$_2$, 101056-27-3; py, 110-86-1; toluene, 108-88-3.

---

(10) Straub, K. D.; Rentzepis, P. M.; Huppert, D. *J. Photochem.* **1981**, *17*, 419–425.

Contribution from the Department of Chemistry,
Faculty of Science, Shimane University, Matsue 690, Japan

Photoinduced Radical Formation of Bis(phthalocyaninato)lanthanoid(III) in a Solvent Mixture of Dichloromethane and Acetonitrile

Kuninobu Kasuga,* Hideharu Morimoto, and Motonori Ando

Received December 26, 1985

A bis(phthalocyaninato)lanthanoid(III) complex, PcLnPcH (Pc = phthalocyanine dianion; Ln = lanthanoid(III) cation), has received considerable attention for its characteristic properties such as electrochromism[1] and electrical conductivity.[2] The structure of bis(phthalocyaninato)neodymium(III) was recently revealed to be of a sandwich type from an X-ray diffraction study.[3] Application of the PcLuPcH complex to an electrochromic display has also been studied by Nicholson and her co-workers.[4] The electrochromism is attributable to generation of various π-radical species that show different bright colors depending upon the applied potentials.[5]

Previously, we reported that a green radical was prepared from a blue PcNdPcH complex in a solvent mixture of dichloromethane and methanol with a chemical oxidant such as *p*-benzoquinone.[6] Upon photoirradiation, the radical was also generated from the blue PcLnPcH complex in the solvent mixture of dichloromethane and acetonitrile. We report here the photoinduced oxidation of the bis(phthalocyaninato)lanthanoid(III) complexes.

Experimental Section

The PcLnPcH complex, where Ln is La(III), Nd(III), Lu(III), or Y(III), was prepared and purified by the method described before.[7] The solvents used for the measurements were reagent grade and were used without further purification. The sample solution in a glass cell with a 1-cm light path length was purged by nitrogen gas and was irradiated with an Eikoshia PIH 300-W high-pressure Hg lamp through a Pyrex filter at 20 ± 2 °C (the cell was situated 3 cm away from the light

---

(1) Moskalev, P. N.; Kirin, I. S. *Russ. J. Phys. Chem. (Engl. Transl.)* **1972**, *46*, 1019.

(2) ter Harr, L. W.; Hatfield, W. E.; Tsutsui, M. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 181.

(3) Kasuga, K.; Tsutsui, M.; Petterson, R. C.; Tatsumi, K.; Opdenbosch, N. V.; Pepe, G.; Myer, E. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4836.

(4) Nicholson, M.; Galiardi, R. V. *Gov. Rep. Annunce. & Index (U.S.)* **1977**, *77*, 112. Nicholson, M.; Weismuller, T. P. *Ibid.* **1983**, *83*, 6250 and references cited therein.

(5) Corker, G. A.; Grant, B.; Clecak, N. J. *J. Electrochem. Soc.* **1979**, *126*, 1339.

(6) Kasuga, K.; Ando, M.; Morimoto, H. *Inorg. Chim. Acta* **1986**, *112*, 99.

(7) Misumi, S.; Kasuga, K. *Nippon Kagaku Zasshi* **1971**, *92*, 335.

0020-1669/86/1325-2478$01.50/0

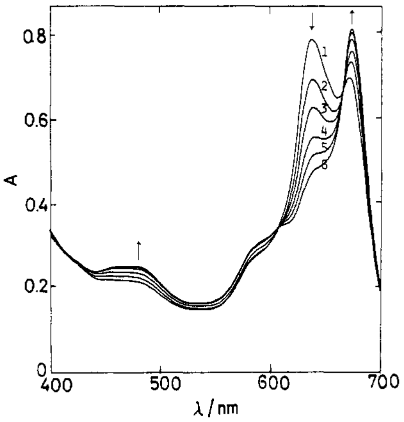

Figure 1. Spectral changes during the oxidation of PcNdPcH in the acetonitrile solution containing 60% (v/v) dichloromethane with irradiation light of λ >320 nm ($[\mathrm{PcNdPcH}]_0 = 1.00 \times 10^{-5}$ mol dm^{-3}): (1) 20 s, (2) 5 min 30 s, (3) 17 min, (4) 25 min, (5) 40 min, and (6) 60 min after irradiation.

Table I. Relative Quantum Yields for Radical Formations under Photoirradiation in the Solvent Mixture of Dichloromethane and Acetonitrile

run	conditions	quantum yield
	$[\mathrm{PcNdPcH}]_0 = 1.00 \times 10^{-5}$ mol dm^{-3}	
1	40% (v/v) CH_2Cl_2	0.51
2	60% (v/v) CH_2Cl_2	0.70
3	70% (v/v) CH_2Cl_2	0.90
4	80% (v/v) CH_2Cl_2	1.00
	$[CH_2Cl_2]_0 = 6.27$ mol dm^{-3}	
5[a]	PcNdPcH	0.64
6[a]	PcYPcH	0.81
7[a]	PcLuPcH	1.00

[a] $[\mathrm{complex}]_0 = 1.00 \times 10^{-5}$ mol dm^{-3}.

source). Electronic spectra were recorded on a Hitachi 124 spectrophotometer. The ESR spectra (X-band) were measured at room temperature with a JEOL-1X spectrophotometer.

Results and Discussion

The solvent mixture of dichloromethane and acetonitrile containing the PcNdPcH complex was irradiated with a wavelength >320 nm (Figure 1). Upon irradiation, absorption bands at 334 and 636 nm of PcNdPcH were shifted to 320 and 676 nm, respectively, with the appearance of a new band around 470 nm characteristic of radical phthalocyanine;[8,9] isosbestic points were found at 330, 357, 600, and 665 nm. The final spectrum was identical with that of the radical PcNdṖc species.[7,8] The radical was also confirmed by an ESR measurement; the solution after irradiation showed an intense ESR signal at $g = 2.00$, which is typical of a radical species of phthalocyanine.[5,6,9]

Without dichloromethane, the radical was not generated under photoirradiation. Relative quantum yields in the presence of various concentrations of dichloromethane are shown in Table I.[10] The relative quantum yield straightly increases with an increase of the concentration of dichloromethane. The lanthanum(III) complex decomposed under irradiation with light of λ > 320 nm. It is improbable that dichloromethane is excited with a light of λ > 320 nm, and hence the PcLnPcH complex absorbs light energy at first and might form an exciplex with dichloromethane. The excited electron is then transferred to dichloromethane, resulting in radicals:

$$\mathrm{PcLnPcH} + CH_2Cl_2 \xrightarrow{h\nu} (\mathrm{PcLn\dot{P}cH})^+ + \dot{C}H_2Cl + Cl^-$$

$$(\mathrm{PcLn\dot{P}cH})^+ \rightarrow \mathrm{PcLn\dot{P}c} + H^+$$

The similar photooxidations of ruthenocene, a carbonyl(η^5-cyclopentadienyl)iron(I) tetramer, and metal porphyrins in the presence of halocarbons have been reported.[11-13]

The relative quantum yield increases with decreasing ionic radius of the lanthanoid(III) ion (Table I). Since the bond length between the lanthanoid(III) ion and the nitrogen atoms in the macrocycles is shortened with the decrease of the ionic radius, the π–π interaction of the two ring systems must become stronger in the order of the neodymium(III), yttrium(III), and lutetium(III) complexes. This might raise an energy level of the HOMO orbital of the rings, and thus the oxidation of the complex becomes easier in this order.

Acknowledgment. We gratefully acknowledge Dr. Yasuo Kubo for useful discussions and also Professor Yasuo Yamamoto, Shimane University, for his encouragement. This work was supported by a Grant-in-Aid for Scientific Research (No. 60540393) from the Ministry of Education, Science and Culture.

Registry No. PcLaPcH, 11060-90-5; PcNdPcH, 12369-76-5; PcLuPcH, 12369-74-3; PcYPcH, 37239-59-1; PcNdṖc, 76723-41-6; acetonitrile, 75-05-8; dichloromethane, 75-09-2.

---

(8) Chang, A. T.; Marchon, J. *Inorg. Chim. Acta* **1981**, *53*, L241.

(9) Sugimoto, H.; Higashi, T.; Mori, M. *Chem. Lett.* **1982**, 801. Sugimoto, H.; Higashi, T.; Maeda, T.; Mori, M.; Masuda, H.; Taga, T. *J. Chem. Soc., Chem. Commun.* **1983**, 1234.

(10) The yield of the radical after 3 min of irradiation was obtained by measuring the absorbance decrease at 636 nm (Q-band of the starting complex). The relative quantum yield is estimated as a relative value to the largest one in a series of concentration effects of dichloromethane. The relative quantum yield for the ionic radius effect is also estimated in a similar manner.

(11) Borrell, P.; Henderson, E. *J. Chem. Soc., Dalton Trans.* **1975**, 432.

(12) Bock, A.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 1309.

(13) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1984**, *23*, 382.

Contribution from Chemistry Department I,
Inorganic Chemistry, H. C. Ørsted Institute,
University of Copenhagen, DK-2100 Copenhagen Ø, Denmark,
and the Chemistry Department, Royal Veterinary
and Agricultural University, DK-1871 Copenhagen V, Denmark

Weak Chloro Complex Formation by Copper(II) in Aqueous Chloride Solutions

Jannik Bjerrum*[†] and L. H. Skibsted[‡]

Received August 10, 1984

Ramette and Fan[1] have recently criticized our recalculation[2] of spectra and stability constants based on the very reliable spectrophotometric measurements on the copper(II) chloride system made by Schwing-Weill and Khan.[3,4] Ramette and Fan[1] have failed to acknowledge a previous detailed study[5] of copper(II) complex formation in aqueous chloride solution that also forms the basis for our recalculation of Schwing-Weill's data. This is probably the reason for their unjustified criticism and makes it necessary for us to reiterate once more the problems involved.

The reason for our recalculation from the data of Schwing-Weill and Khan was the suspiciously low value for the molar extinction coefficient of the tetrachloro complex at 400 nm ($\epsilon_4 = 216$) compared to that of $CuCl_2$ dissolved in a saturated $CaCl_2$ solution, which has the limiting absorbance $\epsilon^\circ = 950$ at 400 nm. The copper(II) chloride spectra in the UV and in the blue visible region are due to electron-transfer transitions, and as such they are more influenced by the medium than is the case with ligand field spectra.[6] However, there can be no doubt that the limiting molar

---

[†] University of Copenhagen.

[‡] Royal Veterinary and Agricultural University.

0020-1669/86/1325-2479$01.50/0