Inorganica Chimica Acta, 64 (1981) L23–124

The Charge Transfer and Ligand Centered Excited State Photochemistries of the First and Second Row d^6-Transition Metal Phthalocyanines

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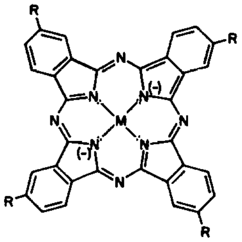
Received August 3, 1981

It was recently reported that cobalt(III) phthalocyanines, Co(ph)X (I) with X = Cl$^-$, Br$^-$, I$^-$, present a significant charge transfer photochemistry which induces the reduction of the metal centre and the oxidation of the axially coordinated ligand X [1]. We have observed now that ultraviolet irradiations of rhodium(III) phthalocyanines (II), isoelectronic with cobalt(III) phthalocyanines, induce the photosubstitution of the axial ligand with $\phi \sim 10^{-2}$ at λ_{excit} = 254 nm. Despite the simplicity of the overall transformation, the intermediates observed by conventional and laser flash photolysis, Figs. 1 and 2, proved to be generated in redox processes, eqns. 1–6 [2]. A primary photogenerated–one electron reduced–rhodium(III)–ligand radical, $\lambda_{max} \sim 510$ nm**, has been observed to transform to a rhodium(II)–phthalocyanine, eqns. 1–3 and Fig. 1. Neither radicals X•, where X• = Cl•, Br• and I•, nor radical anions X_2^-, where X_2^- = Cl_2^-, Br_2^- and I_2^-, have been detected by conventional and laser flash photolysis. This indicates that the axial ligand X$^-$ of Rh(ph)X is not oxidized in a primary charge transfer process. Moreover, scavenging with 1.0–1.0 × 10^{-2} *M* 2-propanol reveals that the acetonitrile solvent is oxidized. The reaction between radicals, generated by the oxidation of acetonitrile, and excess Rh(III) phthalocyanine produces an oxidized Rh(III)–ligand radical which has been characterized by EPR and observed in flash photolysis, eqn. 4 and Fig. 2.



(I) M = Co R = SO$_3$H

(II) M = Rh R = H

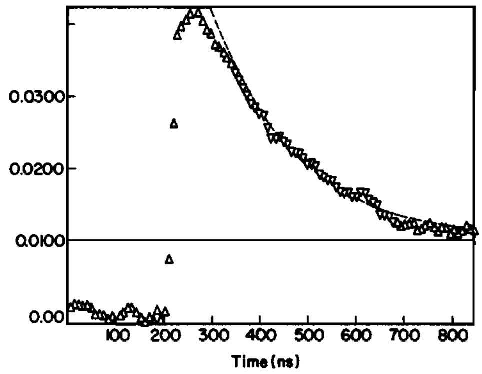


Fig. 1. Characteristic trace obtained in laser flash photolysis, $\lambda_{excit} \sim 337$ nm, of Rh(ph)Br in deaerated CH$_3$CN. The decay of the reduced Rh(III)–ligand radical was followed at λ = 510 nm.

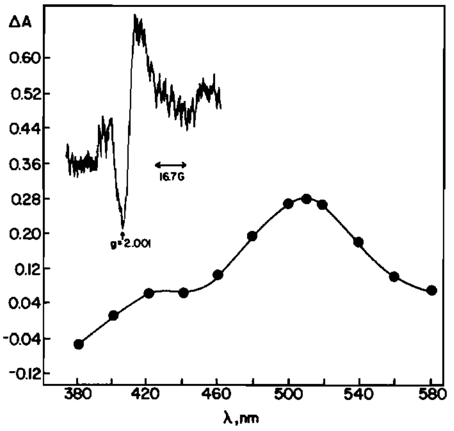


Fig. 2. Transient spectrum determined 50 μs after the irradiation of Rh(ph)Br in deaerated CH$_3$CN. Excitation at $\lambda_{excit} \geq 240$ with 250 Joule/pulse. Inset shows the EPR spectrum obtained under steady state irradiation of Rh(ph)Br in deaerated CH$_3$CN at $\lambda_{excit} \geq 240$ nm.

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**Notice that already characterized phthalocyanine radicals, produced by one electron reduction of phthalocyanine present characteristic absorptions with $\lambda_{max} \sim 500$ nm [1, 3, 4].

This ligand radical species disappears by processes with a second order dependence in transient concentration, eqns. 5 and 6. The proposed mechanism, eqns. 1–6, accommodates the overall photolabilization as well as the observed intermediates.

$$\mathrm{Rh^{III}(ph)X} \xrightarrow{h\nu} {*}\,[\mathrm{Rh(ph)X}] \xrightarrow[\mathrm{CH_3CN}]{} \mathrm{Rh^{III}(ph^{\bullet}{-}H)X} + \dot{\mathrm{C}}\mathrm{H_2CN} \qquad (1)$$

$$\mathrm{Rh^{III}(ph^{\bullet}{-}H)X} \rightleftharpoons \mathrm{Rh^{II}(ph)} + \mathrm{H^+} + \mathrm{X^-} \qquad (2)$$

$(\lambda_{max} \sim 510\ \mathrm{nm})$

$$\mathrm{Rh^{II}(ph)} + \mathrm{CH_3CN} \rightleftharpoons \mathrm{Rh^{III}(\dot{p}h)(CH_3CN)^-} \qquad (3)$$

$$\dot{\mathrm{C}}\mathrm{H_2CN} + \mathrm{Rh^{III}(ph)X} \xrightarrow{\mathrm{H^+}} \mathrm{CH_3CN} + \mathrm{Rh^{III}(\dot{p}h)X^+} \qquad (4)$$

$$\mathrm{Rh^{III}(\dot{p}h)X^+} + \mathrm{Rh^{II}(ph)} \xrightarrow[\mathrm{CH_3CN}]{} \mathrm{Rh^{III}(ph)X} + \mathrm{Rh^{III}(ph)(CH_3CN)^+} \qquad (5)$$

$$\mathrm{Rh^{III}(\dot{p}h)X^+} + \mathrm{Rh^{III}(\dot{p}h)(CH_3CN)^-} \rightarrow \mathrm{Rh^{III}(ph)X} + \mathrm{Rh^{III}(ph)(CH_3CN)^+} \qquad (6)$$

In addition, the nature of the intermediates indicates that they are originated in the primary oxidation of acetonitrile by excited phthalocyanine, eqn. 1. Such a reaction is similar to one previously reported for copper(II) phthalocyanine [4]. In this regard, the differences between the (nπ*) photochemistry of the Rh(III) and the charge transfer photochemistry of Co(III) compounds can be attributed to the large energies associated with the reduction of Rh(III) to Rh(II) in comparison to those required with structurally related Co(III)/Co(II) couples. These differences in the reduction potentials justify that ligand to metal charge transfer states, namely $X^- \rightarrow$ Rh(III), are displaced to energies larger than those of the photoreactive (nπ*) state in Rh(ph)X.

Acknowledgement

The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2255 from the Notre Dame Radiation Laboratory.

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