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The effect of mixed phthalocyanine–porphyrin aggregation on the photoreduction of manganese porphyrins

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Abstract

The ultraviolet photochemistry of mixed porphyrin···phthalocyanine aggregates containing (*meso*-tetramethylpyridylporphyrinato)manganese(III) chloride has been investigated. Photolysis results in the photoreduction of the manganese center in the presence of a radical scavenger. Aggregation has a pronounced effect on the quantum yield of the process. The results are explained in terms of a charge transfer between the component macrocycles. The stability of the photoproduct is markedly influenced by the presence of phthalocyanines as evidenced by the rate of reoxidation of the photoproduct by oxygen.

Introduction

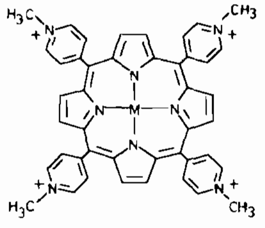
Porphyrins and porphyrin-like macrocyclic compounds perform a myriad of functions in biological systems. In many of the proteins involved with the processes of respiration and photosynthesis, two or more macrocycles are found in close proximity. It has been suggested that a coplanar arrangement of the macrocycles is an essential feature for the electron transfer process [1].

A number of methods involving synthetic porphyrins have been developed to model the interactions between macrocycles found in these complicated biomolecules. These include covalently linking two or more porphyrins [2], structural and magnetic characterization of 'face-to-face' dimers in the solid state [3], and pairing porphyrins having oppositely charged substituents about their peripheries [4]. This last method is particularly intriguing as the components of the aggregates can be varied at will. Unfortunately, the aggregates formed have limited solubility and so solution studies are restricted.

Porphyrins and phthalocyanines bearing oppositely-charged substituents form soluble aggregates of known stoichiometry in water [5] and polar organic solvents [6]. In aqueous solution, the heteroaggregates were found to be composed of one porphyrin and one phthalocyanine in all cases examined. Further, the equilibrium constants associated with the formation of the mixed dimers were found to be independent of the coordinated metal ions but very much dependent on the ionic strength of the medium, suggesting that the driving force for aggregate formation is of an electrostatic nature [5].

The effect which aggregate formation has on the photochemical properties of the component macrocycles is of particular interest. Tran-Thi and Gaspard have suggested that aggregate formation imparts a peculiar stability to mixed aggregates possessing cationic zinc phthalocyanine and anionic manganese porphyrin components [7].

Our efforts have focused on aggregates employing Mn(III) porphyrins and Ni(II) or Cu(II) phthalocyanines. We report herein the effect of phthalocyanine on the photoreduction of heterodimers composed of Mn(III) tetramethylpyridylporphyrin (**I**) and Ni(II) or Cu(II) tetrasulfophthalocyanines (**II**), hereafter referred to as M(P) and M(Pc), respectively.



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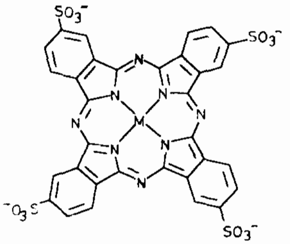

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Experimental

Mn(III)(P)Cl_5 was prepared by the method of Harriman and Porter [8]. The sodium salts of Ni(II) and Cu(II) tetrasulfophthalocyanine were purchased from Aldrich Chemical Company, purified via repeated recrystallization from aqueous solution by addition of ethanol and dried over phosphorous pentoxide under vacuum.

For continuous photolysis studies, a low pressure Hg spectral lamp was used for irradiation at 254 nm. The intensity of the source was calibrated via ferrioxalate actinometry. In a typical photolysis run, aliquots of aqueous solutions of both macrocycle components and methanol, ethanol or 2-propanol were added via a syringe to a 1 cm quartz cell equipped with a 2 mm side-arm cell and a Teflon stopcock. The solution was deaerated by bubbling with N_2 and stirred magnetically in the 1 cm cell while photolyzing for 2–5 min intervals. Spectral changes were monitored by transferring the solution to the 2 mm side-arm cell and obtaining the absorption spectrum with a Hewlett-Packard 8451A diode array spectrophotometer. The monitoring source was filtered to remove light below 300 nm to prevent photolysis of the sample.

The yield of Mn(II)(P) was determined by monitoring spectral changes as a function of irradiation time. Formaldehyde yield was investigated by the chromotropic acid procedure [9] after distilling photolyzed samples in a vacuum line. At no time were photolyzed samples exposed to the atmosphere.

Kinetics data for O_2 oxidation of the reduced porphyrin were obtained by monitoring the decrease in absorption of bands associated with the free Mn(II)(P) or reduced aggregate as a function of time immediately following the introduction of O_2 via syringe.

Results and conclusions

The aqueous photochemistry of Mn(III) porphyrins has been well characterized by Harriman and Porter [8] who found that visible and near UV photolysis yielded the corresponding Mn(II) porphyrin in the presence of a suitable hydrogen donor. We have found that 254 nm excitation results in a similar photoreduction. Further, the presence of Ni(Pc) has a pronounced effect on the quantum yield.

Figure 1 shows the spectral changes accompanying the photolysis of a 7.5 M methanol solution 10^{-4} M in both Mn(III)(P) and Ni(Pc). The band at 482 nm is associated with the 1:1 heteroaggregate. The band growing in at about 456 nm corresponds to the production of a Mn(II)(P)···Ni(II)(Pc) aggregate as evidenced by similar spectral changes resulting from chemical reduction with sodium dithionite. No spectral changes accompany photolysis in the absence of a radical scavenger. Photoreduction was found to occur in the presence of methanol, ethanol or 2-propanol. The presence of the three clean isosbetic points in the region of the spectrum shown in Fig. 1 strongly suggests that only two principal species are present. Further, the spectral changes are quantitatively reversed upon addition of O_2 to the system. Formaldehyde is detected in a yield one-half that of Mn(II).

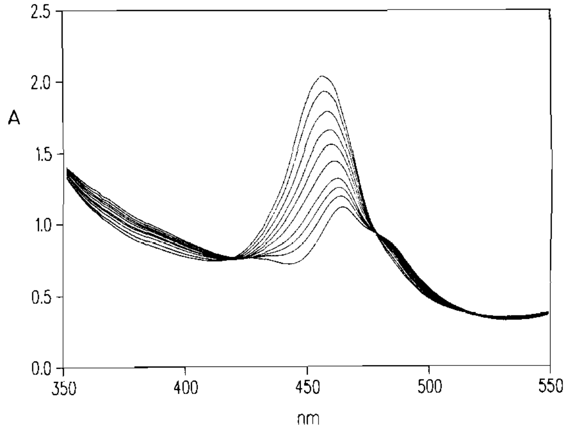

Fig. 1. Spectral changes accompanying the 254 nm photolysis of the 1:1 Mn(P):Ni(Pc) aggregate in 7.5 M methanol. Spectra were obtained at 5 min intervals.

Analyses for free Ni or macrocycle degradation products were negative. Similar results are obtained when Cu(II)(Pc) is employed; however, the rate of reoxidation of the porphyrin component is markedly slower. We are currently investigating this phenomenon. The results of quantum yield studies are reported in Table 1.

The role of the phthalocyanine is more complex than simply a competitor for photons. This is evidenced by the relationship between the quantum yield and the P:Pc ratio or added electrolyte concentration. Equilibrium constants for porphyrin–phthalocyanine aggregates of this nature have been estimated to be 10^5–10^7 [5, 6]. However, the position of the equilibrium has been shown to be very much dependent on the ionic strength of the medium, so that the aggregates disassociate in the presence of added electrolytes. This has been explained in terms of both the decrease in the charge attraction between the oppositely-charged macrocycles and the concomitant increase in self-aggregation exhibited by the phthalocyanine component [5]. This is represented by the following complex equilibria

$$\mathrm{Mn(P)^{5+} + Ni(Pc)^{4-} \overset{K_1}{\rightleftharpoons} [Mn(P)\cdots Ni(Pc)]^{+}}$$

TABLE 1. Quantum yield (Q.Y.) of Mn(II)(P)

[Mn(P)]	[Ni(Pc)]	[MeOH]	[NaCl]	Q.Y.[a]
1.0×10^{-4}	0	5.0	0	1.1×10^{-3}
1.0×10^{-4}	0	5.0	1.0	9.2×10^{-4}
5.0×10^{-5}	5.0×10^{-5}	5.0	0	7.2×10^{-4}[b]
5.0×10^{-5}	5.0×10^{-5}	5.0	0.25	5.1×10^{-4}
5.0×10^{-5}	5.0×10^{-5}	5.0	1.0	2.2×10^{-4}
5.0×10^{-5}	5.0×10^{-5}	2.5	0	3.5×10^{-4}
5.0×10^{-5}	5.0×10^{-5}	1.0	0	3.5×10^{-4}
5.0×10^{-5}	1.0×10^{-4}	5.0	0	3.0×10^{-4}
5.0×10^{-5}	2.5×10^{-5}	5.0	0	4.8×10^{-4}

[a] The quantum yield is defined as the ratio of the moles of Mn(II)(P)···Ni(Pc) produced to the moles of photons absorbed by the solution. All values are reproducible to within 10%. [b] A quantum yield of 3.8×10^{-4} was obtained for formaldehyde under these conditions.

$$2\mathrm{Ni(Pc)}^{4-} \overset{K_2}{\rightleftharpoons} [\mathrm{Ni(Pc)}]_2^{8-}$$

The quantum yield for the reduction of Mn(P) in solution with a 1:1 P:Pc ratio shows a marked dependence on the degree of aggregation as evidenced by the decrease in quantum yield accompanying the increase in NaCl concentration (see Table 1). Further, for solutions having no excess electrolyte, the quantum yield is maximized when the P:Pc ratio is 1:1. When Ni(Pc) is in excess, the amount of light available for excitation of the aggregate is diminished. When Mn(P) is in excess, both the free porphyrin and the aggregate compete for photons. Note, however, that irradiation of the solution with excess porphyrin gives a quantum yield smaller than that obtained in the absence of phthalocyanine. Although these observations do not rule out the possibility that the photoactive species is free Mn(III)(P), they strongly suggest that the light absorbing species which initiates the photochemical process is the aggregate rather than one of the free components, both of which have appreciable molar absorptivities at 254 nm.

The following scheme accounts for our observations, where charges have been omitted for clarity

$$\mathrm{Mn(III)(P)\cdots Ni(II)(Pc)} \overset{h\nu}{\rightleftharpoons} \mathrm{Mn(II)(P)} + \mathrm{Ni(II)(Pc\cdot^{+})}$$

$$\mathrm{Ni(II)(Pc\cdot^{+})} + \mathrm{CH_3OH} \longrightarrow \cdot\mathrm{CH_2OH} + \mathrm{Ni(II)(Pc)} + \mathrm{H^+}$$

$$2\cdot\mathrm{CH_2OH} \longrightarrow \mathrm{CH_3OH} + \mathrm{H_2CO}$$

$$\mathrm{Mn(II)(P)} + \mathrm{Ni(II)(Pc)} \rightleftharpoons \mathrm{Mn(II)(P)\cdots Ni(II)(Pc)}$$

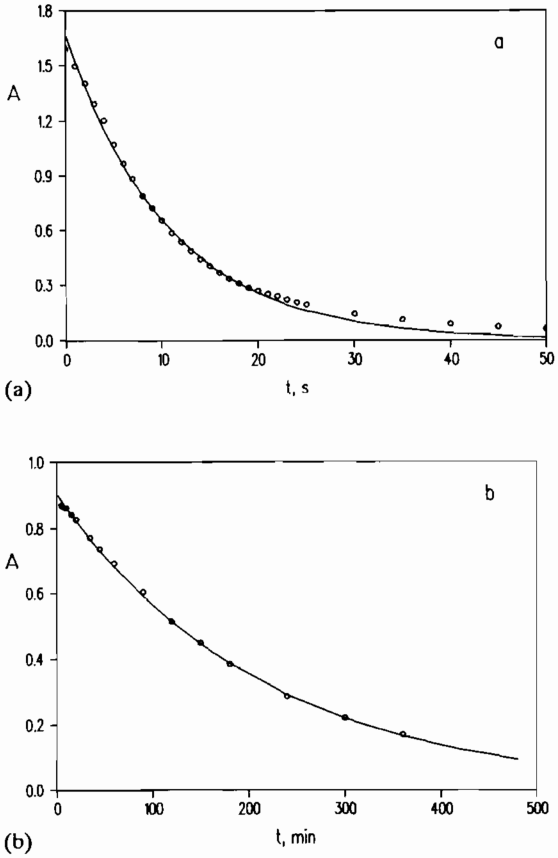

Fig. 2. Kinetic traces displaying the O_2 oxidation of Mn(II)(P) to Mn(III)(P) without (a) and with (b) Ni(Pc) present. For both runs, $[\mathrm{Mn(II)(P)}]=1.0\times10^{-4}$ and the methanol concentration was 5.0 M. In (b), $[\mathrm{Ni(Pc)}]=2\times10^{-4}$. The solid lines are first-order fits of the data.

The process whereby methanol scavenges the radical and which leads to the observed reduction of manganese competes with the back reaction of the reduced porphyrin and oxidized phthalocyanine. At greater concentrations, the scavenger competes with this reaction with increasing effectiveness (see Table 1).

The presence of phthalocyanine has a profound influence on the stability of the photoproduct as evidenced by the disparity in the reaction rates of Mn(II)(P) with O_2 in the absence and presence of Ni(Pc).

[Mn(P)]	[Ni(Pc)]	k_{obs} (s^{-1})
2×10^{-4}		9.3×10^{-2}
1×10^{-4}	1×10^{-4}	2.7×10^{-4}
1×10^{-4}	2×10^{-4}	7.4×10^{-5}

The observed data and first-order fits are shown in Fig. 2 for Mn(II)(P) alone and in the presence of Ni(Pc), respectively. The Mn(II)(P) was generated by 10 min photolysis at 254 nm. Similar results are obtained when the corresponding Cu(II) phthalocyanine is employed and for a 1:1 mix $k_{obs}=5\times10^{-5}$ s^{-1}. The stabilization mechanism may involve steric protection of the reduced porphyrin from oxygen or aggregation may stabilize an oxygen adduct which decays to the observed Mn(III)(P)···Ni(Pc) aggregate as the rate-determining step. At this time, we have no evidence for the existence of a long-lived oxygen adduct.

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References

1 F. R. Salemme, *J. Mol. Biol., 102* (1976) 563; T. L. Poulos and J. Kraut, *J. Biol. Chem., 255* (1980) 10322; T. L. Paulos and A. G. Mauk, *J. Biol. Chem., 258* (1983) 7369; M. W. Makinen, S. A. Schichman, S. C. Hill and H. B. Gray, *Science, 222* (1983) 929.
2 J. R. Collman, C. S. Bencosme, C. E. Barnes and B. D. Miller, *J. Am. Chem. Soc., 105* (1983) 2704; C. K. Chang, *J. Heterocycl. Chem., 14* (1977) 1285; N. E. Kagan, D. Mauzerall and R. B. Merrifield, *J. Am. Chem. Soc., 99* (1977) 5484.
3 W. R. Scheidt and Y. J. Lee, *Struct. Bonding (Berlin), 64* (1987) 1.
4 E. Ojadi, R. Selzer and H. Linschitz, *J. Am. Chem. Soc., 107* (1985) 7783.
5 D. K. Geiger and C. A. Kelly, *Inorg. Chim. Acta, 154* (1988) 137.
6 S. Radzki, S. Gaspard and C. Ginnotti, *J. Chem. Res. M,* (1986) 3101.
7 T.-H. Tran-Thi and S. Gaspard, *Chem. Phys. Lett., 148* (1988) 327.
8 A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. II, 75* (1979) 1543.
9 J. C. Speck, *Methods in Carbohydrate Chemistry,* Vol. I, Academic Press, London, 1962, p. 443.