Photoreactions of Metalloporphyrins in Supported Monolayer Assemblies and at Assembly–Solution Interfaces. Reductive Addition of Palladium Complexes with Surfactant and Water-Soluble Dialkylanilines[1]

Janet A. Mercer-Smith and David G. Whitten*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received February 20, 1979*

Abstract: The photoreactivity of surfactant metalloporphyrins anchored in organized multilayer assemblies formed from sequential deposition of monolayer films has been investigated. Although metal complexes studied include the zinc and tin porphyrins, the most extensive results have been obtained with palladium(II) complexes. Two palladium(II) porphyrins have been used; one resides in a hydrophilic site in films and multilayer assemblies while the other occupies a hydrophobic site. The anchored porphyrins undergo reduction and reductive photoaddition reactions with a number of reagents penetrating the assemblies in interfacial processes from a contacting aqueous solution. The palladium porphyrins yield reductive photoadducts with *N,N*-dimethylaniline (DMA) analogous to their reaction with the same reagent in homogeneous solution; the results indicate that DMA readily penetrates and reacts in both hydrophilic and hydrophobic regions of the supported multilayer. Studies with the surfactant analogue of DMA, *N,N*-dioctadecylaniline (DOA), also indicate reductive photoaddition for the palladium porphyrins and DOA when both are incorporated into supported multilayers. Results obtained with assemblies formed by a number of different deposition sequences indicate that considerable migration of supposedly "anchored" reagents such as DOA can occur in the assemblies.

Introduction

There have been a number of reports of reactions occurring with one or more reagents incorporated in an organizate such as a micelle, monolayer film, or vesicle in which pronounced changes from homogeneous-phase processes are observed either in rates or products or in both.[2-10] In some cases the differences have been ascribed to orientation or solvation effects,[6,10-12] while in other cases limited or enhanced penetration by solutes[13-19] has been indicated to be the controlling factor. This paper deals with reactions occurring within multilayer assemblies supported on glass; the investigations reported include both reactions occurring with "dry" assemblies and those in which the supported assembly is contacted with an aqueous solution containing a potentially reactive solute. The reaction under investigation in these studies is the photoreduction of metalloporphyrins consecutively to chlorin (dihydroporphyrin) and isobacteriochlorin (tetrahydroporphyrin) derivatives.[20-27] The bulk of the work described involves anchored surfactant palladium porphyrins as the excited substrates and dialkylanilines as the reductants. For these reagents, as has previously been found in solution investigations,[27] the major process involves reductive addition of the aniline to the palladium porphyrin.

Considerable evidence has been obtained indicating that in both monolayer films of saturated fatty acids and related surfactants at an air–water interface and in glass-supported multilayers formed by transferral of the highly compressed films a well-defined ordered assembly obtains in which the hydrocarbon chains are in an all-trans (zigzag) arrangement with spacings close to those occurring in crystalline fatty acids or hydrocarbons.[28-34] Although the multilayer assemblies are indicated to have a closely packed, highly ordered structure, there is abundant evidence that these assemblies can be penetrated by a variety of reagents in processes which may or may not result in permanent disruption of the ordered arrangement.[13-16,29] A number of investigations have established that small neutral molecules such as O_2, CO, N_2, and NO can readily penetrate through several multilayers and react at both hydrophilic and hydrophobic sites.[15,16,35,36] There have also been indications that small, neutral organic molecules can penetrate both hydrophobic and hydrophilic regions when the supported multilayer is exposed to an aqueous solution or vapor containing the reagent; in a number of cases rapid reaction has been observed. In one investigation of these phenomena, Kuhn and co-workers found that a coupling reaction between an anchored diazonium ion and 8-hydroxyquinoline could be mediated by immersing supported multilayers of the diazonium salt into aqueous solutions containing the quinoline.[29,37,38] The anchored salt was found to react rapidly even when the multilayer assembly contained several layers of fatty acid between the layers of salt and the aqueous solution. That little or no permanent alteration of the assembly occurred during the penetration and reaction was indicated by the subsequent layering of a surfactant fluorescent dye–fatty acid mixture and a study of fluorescence quenching by the newly formed azo dye.[37,38] The extent of fluorescence quenching obtained showed the expected dependence on distance between donor and acceptor as determined by the number and length of intervening fatty acid hydrocarbon chains. In contrast to the results obtained with neutral solutes, it has been found that charged species such as metal ions and even some organic ions generally penetrate only hydrophilic regions of multilayer assemblies or adsorb onto the surface of the assembly, in some cases forming an outer monolayer having organization similar to, but not identical with, layers transferred by the Langmuir–Blodgett technique.[14,29,37-39]

In the present study we have investigated photoreactions of assembly-anchored metalloporphyrins in different sites with a variety of reagents. Not surprisingly our results also indicate that small neutral organics can readily penetrate multilayer assemblies and react well in interfacial processes under conditions where ionic reagents are ineffective. What is perhaps a more surprising result of this study is the finding that relatively large, apparently surfactant or anchored components of assemblies can also migrate through several layers of fatty acid and react in both "dry" and aqueous solution-contacted supported multilayers. These results, together with other recent studies,[40] emphasize the structural dichotomy of supported multilayers between near-crystalline order and liquid-like fluidity.

Experimental Section

Preparation and Purification of Materials. The *meso*-tetra(4-carboxyphenyl)porphyrin tetraoctadecyl ester (TCPTOE) was prepared by methods described elsewhere.[41] The $\alpha,\alpha,\alpha,\alpha$-tetraamino-

0002-7863/79/1501-6620$01.00/0 © 1979 American Chemical Society

phenylporphyrin and its hexadecyltetraamide (H_2PF,THA) were prepared by methods developed by Collman and co-workers.[42] Bis(benzonitrile)palladous chloride used in metalating porphyrins was synthesized by a modification of the method of Kharasch, Seyler, and Mayo.[43] Palladous chloride (0.557 g) was mixed with 25 mL of reagent benzonitrile and heated to 100 °C. The yellow-green color of the solution changed to a deep red-brown upon heating, and a small amount of black, powdery material remained at the bottom of the beaker. The hot solution was rapidly filtered, hot benzonitrile was added to the black, powdery residue, and heating was continued; this resulting red-brown solution was also filtered. Both filtrates were combined and hexanes were added. Orange-yellow crystals were obtained upon cooling. The total yield of two crops (1.07 g) was 88%. The palladium complex of TCP-TOE was prepared by the method of Hopf.[41] For forming the palladium complex of H_2PF,THA; PdPF,THA benzene was used as the metalation solvent so that the reaction would be accomplished at lower temperatures, thus avoiding appreciable thermal interconversion of the atropisomers.[42] H_2PF,THA (0.103 g)[44] and bis(benzonitrile)palladous chloride (0.0646 g) were placed in a 50-mL round-bottom flask fitted with a reflux condenser, and reagent benzene (25 mL) was added.[45] The mixture was heated to reflux under deoxygenated nitrogen. Optical absorption spectra were taken at intervals until the free base satellite bands ceased to decrease relative to the intensity of the bands of the metalated porphyrin. After 4 h a new band at 608 nm, possibly due to metallochlorin, appeared, and heating was discontinued. The reaction mixture was allowed to stand for 12 h under nitrogen. The metalloporphyrin was purified by chromatography on preparative 500-μm silica gel thin layer chromatography plates (Analtech) using 97.6% chloroform and 2.4% diethyl ether. The fluorescent free base moved ahead of the metalated porphyrin, but a second set of free base and metalloporphyrin bands moved more slowly. This was probably due to the atropisomers formed during refluxing in the metalation reaction. Further purification was accomplished by chromatography of a 94.2:2.4:2.4 chloroform-diethyl ether-hexane solution on a medium-pressure column packed with Woelm silica gel set with the same eluent. A small amount of the first fraction which came off the column was slightly fluorescent, and the last band off the column had a small amount of metallochlorin in it. Both the middle fraction from the medium-pressure column and the metalloporphyrin purified by preparative thin layer chromatography alone were crystallized from chloroform-methanol and dried in a vacuum desiccator. Little difference could be detected between the two fractions by either UV-visible or emission spectroscopy. Small, red microcrystals resulted from the medium-pressure chromatography purification, while the material purified by preparative thin layer chromatography alone was less crystalline. The total yield (0.048 g) for these two fractions was 43%. The tin complex, SnPF,THA$(Cl)_2$, was synthesized by a slight modification of the method of O'Rourke and Curran.[44] *N,N*-Dimethylaniline (Aldrich, 99%) was vacuum distilled immediately before use. Arachidic (1-eicosanoic) acid (Analabs, Inc.) was used as received. *N,N*-Octadecylaniline was received as a gift from Dr. D. Möbius and used as received. Solvents were purified as described previously. Triply distilled water was used for monolayer studies and for preparation of solutions contacting deposited monolayer assemblies in interfacial studies.

Monolayer Techniques. The general methods used for preparing films and assemblies and for the preparation of glass slides are described elsewhere.[29] For the studies described here all slides in analytical studies (1 × 4 cm) were precoated with cadmium arachidate (five layers) at a speed of 0.02 cm/s and a pressure of 30 dyn/cm. This was followed with deposition of successive layers of 1:5 metalloporphyrin-arachidic acid coated at a speed of 0.014 cm/s and a pressure of 20 dyn/cm. Since the ease of photoreduction of the metalloporphyrins in spread films or monolayer assemblies was not known at the outset of the experiments, all spreading and coating were performed in dim light. For product analysis studies, 5 × 10 cm slides were precoated with one layer of cadmium arachidate; this reduction in the number of sublayers did not seem to make any difference in the ability to coat successive layers of surfactant materials. The PdPF,THA was diluted 1:2.5 with arachidate since the pure porphyrin formed a spread film which was too fragile to coat. A 1:2.5 *N,N*-dioctadecylaniline-arachidate mixture was used for the same reason. For studies in which porphyrin and amine were incorporated in the same layer a 1:1:2.5 mixture, PdPF,THA-*N,N*-dioctadecylaniline-arachidate, was used. The spread films from these solutions were allowed to "rest" for 1-2 min before compressing to 20 dyn/cm pressure; the compressed monolayer was allowed to rest for an equal amount of time prior to coating the slides with the speed of 0.014 cm/s. When alternate layers or cycles of PdPF,THA and *N,N*-dioctadecylaniline were coated, the surface of the water was cleaned between changes of surfactant materials by aspirating the spread film, spreading and aspirating a new film of arachidate, and then spreading the next film of surfactant to be deposited. For the single-layer studies a hydrophilic surface of PdPF,THA-arachidate was spread and coated at a speed of 0.014 cm/s and a pressure of 20 dyn/cm. After the slides had been lowered through this spread film at a constant film pressure, they were dropped into small beakers positioned directly below the slide clamps. The spread film was aspirated, and a layer of arachidate was spread and aspirated to clean the surface of the water before the beakers containing the slides were transferred underwater to multislide square Pyrex or quartz cells and fitted into a slotted Teflon slide holder. For interfacial studies, DMA was pipetted into the cell to make a 2.5×10^{-3} M solution. A serum cap was placed over the neck of the cell, and the solution was bubble-deaerated for 20 min with argon which had passed through a chromous oxygen purge. After deaeration, a piece of electrical tape was placed over the top of the serum cap. The same bubble-deaerating procedure was used for all the monolayer studies. Reagent chloroform was used as solvent for spreading the films in all cases. Surface pressure-area measurements (isotherms) and transfer ratios were obtained using an electronically controlled circular Teflon trough and Wilhelmy balance, as described by Fromherz.[46]

Photochemical Studies. Irradiations of porphyrins in solution and in deposited assemblies with visible light were carried out using a General Electric (H100PSP44-4) floodlamp filtered through 18.5 cm of water in a Pyrex vessel and Corning 3-74 filters. The slides were placed in quartz or Pyrex chambers fitted with a serum cap and purged with argon; the slides were held in place by use of a Teflon holder. In interfacial studies the same chamber was filled with an appropriate aqueous solution which was deaerated by bubbling for ca. 20 min or more with a slower stream of argon.

Analyses. Either a Perkin-Elmer 576 ST spectrophotometer or a Bausch & Lomb spectronic 210 UV spectrophotometer was used for spectral determinations of reactions and for use in Reinecke salt actionometry. A Hitachi MPF-2A spectrofluorimeter equipped with a R446 photomultiplier tube was used for luminescence studies. For medium-pressure liquid chromatography, solvent was pumped by a FMA Lab Pumb Model RP-5Y. The columns were packed with 0.032-0.063-nm Woelm silica gel distributed by ICN Pharmaceuticals, Inc. A scrubber column of 1.5 × 25 cm and a longer column of 1.5 × 10 cm were used. The columns were packed dry by vibrating. Before the metalloporphyrins were injected onto the columns, the columns were flushed with the solvent long enough to remove air. Aluminum foil was wrapped around the columns to protect the light-sensitive compounds.

Results

The monolayer characteristics of the porphyrins used in these studies have been previously determined for the free bases and some metal complexes.[14,15,41] These investigations have indicated that the location of the porphyrin chromophore in films and deposited multilayers is controlled by the number, size, and location orientation of hydrophobic and hydrophilic groups substituting the porphyrin macrocycle. For the "picket fence" porphyrin H_2PF,THA (the $\alpha,\alpha,\alpha,\alpha$ atropisomer in which the *O*-amino groups have been converted to hexadecylamides) the substitution of four relatively large hydrophobic groups on one side of the porphyrin forces the porphyrin to occupy a site in which one face of the porphyrin is in a relatively hydrophilic region at or near the film-water interface in films or a hydrophilic-hydrophilic contact plane in deposited multilayers.[14] In contrast previous studies suggest that the other porphyrin used in these studies, *meso*-tetra(4-carboxyphenyl)porphyrin tetraoctadecyl ester (TCP,TOE), resides in a more hydrophobic site and that the porphyrin ring is probably bent back from the plane of the film or film layer in multilayers.[14,35,41] Since the palladium(II) complexes of porphyrins do not normally strongly coordinate extraplanar ligands,[47] it appears reasonable to assume that the palladium porphyrins

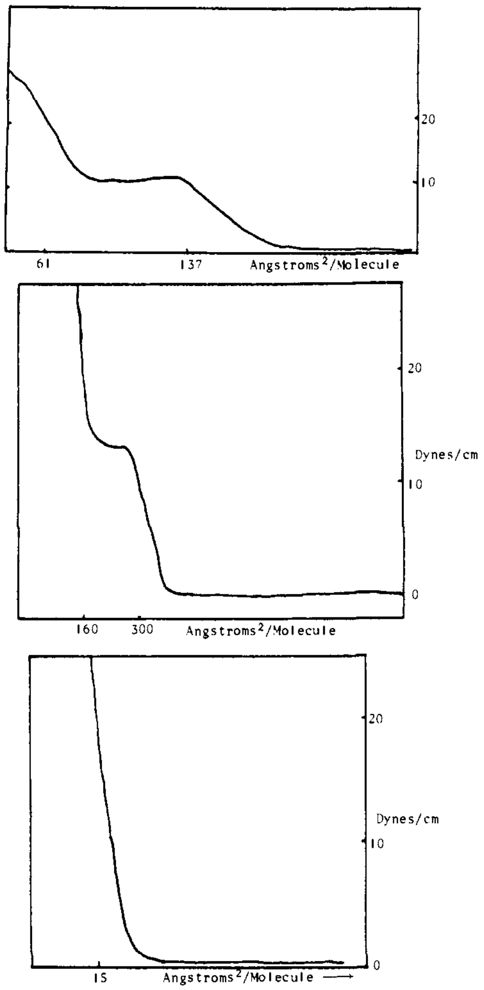
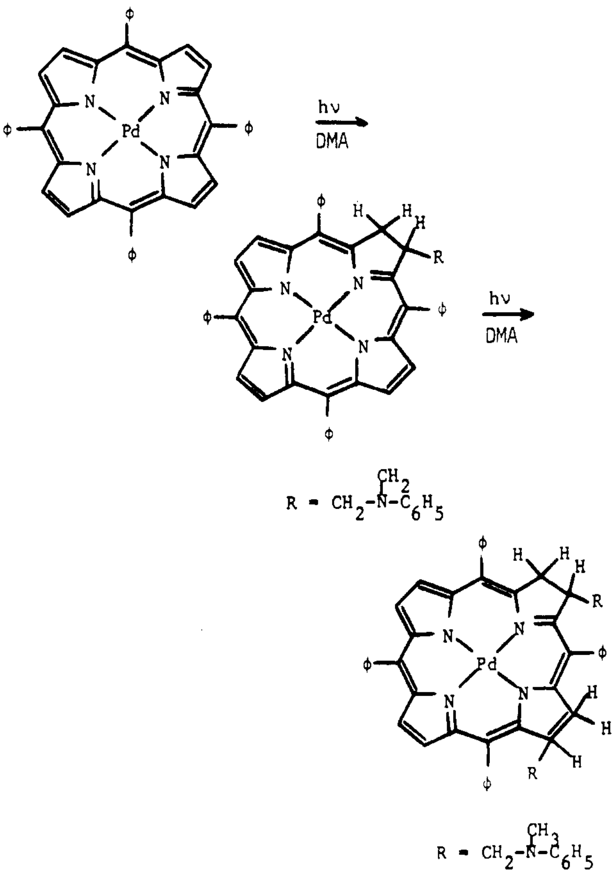


Figure 1. Surface pressure-area isotherms for PDPF,THA and DOA. Upper trace: pure PDPF,THA. Middle trace: PDPF,THA-AA (1:2.5). Lower trace: DOA-AA (1:2.5).

used in this study, PdPF,THA and PdTCP,TOE, would occupy sites in monolayer films and assemblies similar to those of the respective free bases. This expectation is supported by our findings of very similar surface pressure-area characteristics for films of the palladium complexes and free bases in both cases. For PdPF,THA, spreading the pure complex dissolved in chloroform leads to a fragile film whose isotherm (Figure 1) shows liquid-like characteristics and a surprisingly small area of 61 Å^2/molecule at a pressure of 20 dyn/cm. These films cannot be transferred to a glass support so most studies have been made using mixtures of PdPF,THA with arachidic acid (AA). A stable film is formed from 1:2.5 PdPF,THA-AA mixtures which can be compressed up to 30 dyn/cm without collapsing; this film gives a condensed solid isotherm (Figure 1) and a calculated area of 160 Å^2/molecule for the porphyrin in the mixed layer. These films can be transferred to a rigid support to form single or multilayered assemblies; a transfer ratio of 1.0 ± 0.2 (area of film removed from air-water interface divided by area of support covered) was obtained. PdTCP,TOE also gives an isotherm of a condensed solid when spread in mixed films with AA (1:3.5). The film characteristics of the tin and zinc complexes, ZnPF,THA and SnPF,THA(Cl)$_2$, were not thoroughly investigated; however, it was found that mixtures of porphyrin-AA (1:2.5) gave stable films that could be transferred to form single or multiple layered assemblies at pressures of 20 dyn/cm. The surfactant amine used in these studies, *N,N*-dioctadecylaniline (DOA), does not form stable films when introduced to a water surface from chloroform; however mixed films with AA (1:2.5) are stable over the range 0–30 dyn/cm and give an area of 15 Å^2/molecule for the amine and a reasonably sharp isotherm (Figure 1). Although these films could be transferred to glass or quartz slides without difficulty, the transfer ratios (film removed divided by slide area covered) obtained were surprisingly large (1.6–2.0) compared to those obtained with pure AA (0.9–1.0) or mixed porphyrin-AA.

Interfacial Photoreactions. Glass slides containing varying numbers of mixed metalloporphyrin-AA multilayers were immersed in aqueous solutions containing various reducing agents and irradiated with visible ($\lambda > 410$ nm) light. The metalloporphyrin-reducing agent combinations chosen were those which have previously been shown to give photoreduction or reductive photoaddition in homogeneous solution.[20-27] In the interfacial studies irradiation of several of the monolayer-incorporated metal complexes led to characteristic spectral changes consistent with the formation of reduced or chlorin-type products. Table I compares the buildup of these products as determined spectroscopically for several different substrate-reductant combinations. For the palladium porphyrins we have found that in solution irradiation with tertiary amines leads exclusively to reductive addition[27] (eq 1) while



(1)

for the tin and zinc porphyrins irradiation with amines, SnCl$_2$-H$_2$O, or amine-ascorbic acid mixtures may give both adducts and unsubstituted chlorin.[20-26] For both PdTCP,TOE and PdPF,THA it was found that irradiation of the porphyrin in solution with DMA and in monolayers contacted with aqueous DMA solutions led to the same products, as determined chromatographically. Thus in the interfacial reaction of the palladium porphyrin reductive photoaddition is evidently the exclusive process. In "blank experiments" it was found that PdTCP,TOE and PdPF,THA show no photoreduction either dry in argon or in argon-saturated water after more than 24 h of irradiation. When DMA was used as the reducing agent, the concentration of amine in the aqueous phase was kept very low ($<10^{-2}$ M) to prevent deterioration of the assembly due

Table I. Relative Rates of Interfacial Photoreaction for Surfactant Porphyrins in Glass-Supported Multilayers

multilayer composition[a]			contacting solution	% chlorin product[b]	% isobacteriochlorin product[b]
PdTCP,TOE-AA	1:2.5	26 layers	aqueous DMA[c]	2.9	
PdTCP,TOE-AA	1:2.5	4 layers	aqueous DMA	8.8	
PdTCP,TOE-AA	1:2.5	2 layers	aqueous DMA	7.5	
PdPF,THA-AA	1:2.5	12 layers	aqueous DMA	26	3.6
PdPF,THA-AA	1:2.5	2 layers	aqueous DMA	16	3.8
SnPF,THA$(Cl)_2$-AA	1:2.5	12 layers	aqueous DMA	21	16
SnPF,THA$(Cl)_2$-AA	1:2.5	12 layers	satd $SnCl_2$	5.3	
SnPF,THA$(Cl)_2$-AA	1:2.5	4 layers	satd $SnCl_2$	11	
ZnPF,THA-AA	1:2.5	10 layers	aqueous Et_3N[d]	1.3	
ZnPF,THA-AA	1:2.5	10 layers	aqueous Et_3N,[e] ascorbic acid	2.6	

[a] For abbreviations see text; the number of layers per side is given. Multiple slides were used so that absorption was uniform in each experiment. [b] Product yields are measured at 610 and 590 nm for chlorin and isobacteriochlorin, respectively. The yields given are for 1-h irradiation with a 100-W lamp filtered through water and a Corning 3-74 glass filter. [c] 2.5×10^{-3} M DMA. [d] 10^{-3} M triethylamine. [e] 10^{-3} M triethylamine and 10^{-3} M ascorbic acid.

to solubilization of the metalloporphyrin. This appeared not to be a problem with the PdPF,THA, which reduces relatively rapidly to yield both chlorin and subsequently isobacteriochlorin products. However, for SnPF,THA, ZnPF,THA, and PdTCP,TOE, irradiation of the solution-contacted assemblies led to slow decomposition such that only the first reduction could be reliably followed; prolonged irradiation led to some buildup of isobacteriochlorin but with competitive decomposition. The products formed from SnPF,THA and ZnPF,THA could not be characterized by other than by spectroscopic techniques owing to the relatively low yield obtained. However, that they are simple chlorins or reductive addition products is suggested by the observation that little or no reaction occurs in the absence of amine.[48] No hexahydroporphyrin products could be detected with any of the surfactant porphyrins studied. During the photoreduction of the metalloporphyrins, no intermediates could be detected; similar results were found for the palladium porphyrins in solution, but other workers have reported intermediates when tin(IV) porphyrins were reduced by stannous chloride[22,23] and zinc(II) porphyrins were reduced by a combination of amines and ascorbic acid.[24] In agreement with previous solution studies of the zinc porphyrins, a combination of ascorbic acid and triethylamine causes much more reduction than triethylamine alone.[24]

Increasing the number of layers of metalloporphyrin in an assembly slows somewhat the rate of photoreduction of these metalloporphyrins when the reducing agent is dissolved in an aqueous solution contacting the assembly.[49] This effect is more pronounced when SnPF,THA is reduced by stannous chloride than when surfactant palladium porphyrins are reduced by DMA (Table I). The reduction of PdPF,THA produces chlorin product twice as fast and gives more isobacteriochlorin formation in assemblies in which the porphyrin is present only in an outer layer having hydrophilic contact with the aqueous DMA solution; however, assemblies of PdPF,THA covered with zero, two, four, six, and eight layers of cadmium arachidate (AA) reduce at essentially the same rate with aqueous DMA to give identical product distributions.[49] One of the features of the palladium porphyrins which makes them attractive candidates for photochemical investigation is their prominent phosphorescence in solution.[50-52] While PdTCP,TOE shows a weak but readily detectable phosphorescence when incorporated into assemblies, PdPF,THA exhibits a phosphorescence in assemblies that is too weak for any quantitative studies. For PdTCP,TOE the phosphorescence observed in assemblies dry or immersed in argon-purged water is strongly quenched by admission of oxygen or exposure to aqueous DMA as indicated in Table II. The finding that 80% of the emission is quenched by immersion of a slide containing 26 layers of PdTCP,TOE in aqueous DMA indicates that the quenching process is not confined to the outer layers. The addition of aqueous DMA does not change the wavelength of absorption or emission of the PdTCP,TOE.

Table II. Quenching of Palladium Porphyrin Phosphorescence by Amines in Supported Multilayers[a]

sample	quencher	I/I_0
PdTCP,TOE-AA 1:5[b]	O^2	0.6
PdTCP,TOE-AA 1:5	aqueous DMA[c]	0.2
PdTCP,TOE-DOA-AA[d] 1:1:2.5	DOA	0.8
PdTCP,TOE-DOA-AA[e] 1:1:2.5	DOA	0.5

[a] λ_{ex} 466 nm, emission measured at 701 nm, slides contained 26 layers/slide. [b] Dry slides, I_0 values obtained under argon. [c] 2×10^{-3} M DMA in water, solution deaerated with argon; no quenching observed with deaerated water alone contacting the assembly. [d] Dry slides, argon atmosphere compared to slides with AA replacing DOA. [e] Slides immersed in argon-purged water.

Photoreactions of Palladium-Porphyrin-Surfactant Amine Assemblies. To complement the interfacial studies several investigations were carried out with the two palladium porphyrins in films and assemblies containing the surfactant analogue of DMA, *N,N*-dioctadecylaniline (DOA). Irradiation of a film formed from a 1:1:2.5 PdPF,THA-DOA-AA mixture at an air-water interface led to the production of chlorin adduct in very low yield. Irradiation of supported assemblies containing DOA and the surfactant palladium porphyrin was found to produce relatively rapid formation of reductive adducts for several different deposition sequences (Table III). However, comparison of the rates obtained in these studies with those obtained for assemblies contacted with aqueous DMA solutions indicated that the latter reacts faster in almost every case. For example, it was found that PdPF,THA-DOA-AA in a 1:1:2.5 ratio in mixed layers or 1:2.5 PdPF,THA-AA and 1:2.5 DOA-AA in adjacent layers with hydrophilic contact are reduced more slowly than deposited assemblies of PdPF,THA (1:15) with AA in contact with 2.5×10^{-3} M aqueous DMA. As data in Table III indicate, while the relative rates of formation of chlorin product do not differ very much in argon-saturated water, a decrease in rate as the distance is increased between the porphyrin and amine can be seen when the assemblies are irradiated in argon. However, upon long irradiation times, the various configurations of porphyrin and amine studied give approximately the same amounts of chlorin and isobacteriochlorin products whether the assembly is irradiated in argon or argon-saturated water. It was not possible

Table III. Relative Rates of Reductive Photoaddition for Palladium Porphyrins in Multilayers Containing *N,N*-Dioctadecylaniline[a,d]

deposition sequence[b]	rel rate of chlorin product formation: dry-argon purged	rel rate of chlorin product formation: wet-argon purged[c]
=Ⓟ A=	18	16
=Ⓟ O— O— —O —O A=	12	16
=Ⓟ O— O— —O —O O— O— —O —O A=	5	12
Ⓟ= =A	9	14
=Ⓟ =A	4	6
=Ⓟ′ =A		4

[a] Percent of chlorin product formed determined spectrophotometrically after irradiation. [b] The sequence was repeated several times in most cases but sequence shown gives minimum "initial" porphyrin–amine separation. [c] Slides immersed in water and deaerated with argon. [d] =Ⓟ = PdPF,THA; =Ⓟ′ = PdTCP,TOE; —O = AA; =A = DOA.

to compare the products produced in deposited multilayers of PdPF,THA and DOA with those produced in solution owing to the fact that irradiation of the solution mixtures led to the formation of the several atropisomers of PdPF,THA concurrent with photoadduct formation.[53] However, retention times obtained by thin layer chromatography suggested that reductive adducts rather than simple chlorin or isobacteriochlorins were produced in the supported multilayers; moreover, the same product distributions were obtained for the supported multilayer for all deposition sequences used, even in the cases where the assemblies were constructed by depositing several "spacer layers" of arachidate between layers of porphyrin and DOA.

The phosphorescence of PdTCP,TOE was also quenched in supported assemblies containing DOA and the porphyrin deposited in the same layer. Since the quenching was relatively slight (Table II), it was not possible to obtain reliable indication of quenching as a function of the deposition sequence.

Discussion

The finding that DMA in an aqueous solution contacting a monolayer assembly composed of 26 layers of PdTCP,TOE can quench most of the phosphorescence of the metalloporphyrin and react to near completion indicates that DMA can diffuse to the hydrophobic reaction site of this porphyrin and participate in the same type of photoreactions observed in solution.[27] Since PdPF,THA contained in assemblies with eight outer layers of cadmium arachidate reduces at essentially the same rate and gives the same product distribution as PdPF,THA with no outer layers of cadmium arachidate, it appears that DMA rapidly penetrates to the hydrophilic regions of the monolayer assembly where this complex is located and reacts in an analogous fashion. These results are in accord with previous findings that relatively small neutral organic molecules can diffuse through both hydrophilic and hydrophobic regions of monolayer assemblies and attain concentrations sufficiently high to permit photoreaction to occur.[29,36,54] The results seem especially reasonable in view of the finding that in Triton X micelles the equilibrium for DMA between aqueous and surfactant greatly favors the organic surfactant ($K_{eq} = 30$).[55] A similar equilibrium in the interfacial studies with the assemblies contacted with aqueous DMA solutions should result in a relatively high concentration of DMA in the assemblies; its relatively high mobility would be expected to permit reactivity with excited porphyrins in either hydrophilic or hydrophobic sites.

Charged molecules are expected to exhibit different behavior in interfacial processes involving assemblies. Positively charged metal ions can enter assemblies through "edges" or defect channels and then move through the plane formed by a hydrophilic–hydrophilic interface.[15,29,36,54] This method of diffusion through the monolayer assembly by metal ions may contribute to the slow photoreduction of SnPF,THA by stannous chloride in multilayer assemblies. Since the solution photoreduction of SnOEP by stannous chloride[22] occurs with $\Phi = 10^{-4}$ and decomposition of monolayer assemblies of SnPF,THA in the presence of stannous chloride occurs after a few hours of irradiation, it is difficult to determine whether the slow diffusion of Sn^{2+} ions within the assembly retards the reaction.

The results obtained in studies of the photoreaction of assemblies containing the palladium porphyrin and DOA using various deposition sequences are at first inspection a bit surprising since it would be anticipated that for assemblies constructed with several spacer layers between the layers containing porphyrin and amine little reaction should occur. The fact that considerable reaction occurs giving the same products obtained in assemblies where the porphyrin and amine are initially placed in contact indicates that some migration of either amine, porphyrin, or both must be occurring within the assemblies. The fact that arachidate–DOA mixtures show abnormally high transfer ratios is perhaps evidence that some squeezing of the DOA out of the film occurs when the film is transferred from the air–water interface to the supported assembly. The observation that the porphyrin is not readily removed from an outer hydrophilic or hydrophobic layer in multilayer assemblies together with the fact that a "normal" transfer ratio is obtained for porphyrin-arachidate films suggests that it is amine and not porphyrin that migrates in the assemblies. While several recent studies have suggested that little migration occurs in multilayer assemblies and that the spacer layer technique can be used to establish distance dependence for various processes,[29,37,56,57] other studies, especially with unsaturated fatty acids, have indicated that migration of surfactant within multilayer assemblies can occur.[40] In recent studies in which migration was indicated, Whitesides and co-workers found that unsaturated fatty acids which were separated from platinum foil by two spacer layers of saturated fatty acids were hydrogenated.[40] The results of this study of the reduction of the fatty acids suggest a picture of fatty acids supported on platinum foil as thin, viscous, liquid, or liquid-crystalline films. Since multilayer assemblies were previously considered to have fairly rigid, stable structures, the finding that fatty acids can move within the assembly is noteworthy. Since, in the present study, we find pure films of uncharged DOA to be unstable and liquid-like under compression at the air–water interface, it is perhaps not unreasonable to assume that in mixed films of AA and DOA some migration or "squeezing out" of the DOA can occur. In one respect the mobility of DOA in fatty acid multilayers should not be too surprising since DOA can be regarded as simply a homologue of DMA which readily migrates. However, the observation that mixed arachidate–DOA films show essentially condensed solid-like behavior would certainly not in itself indicate or suggest easy migration. These results, then, suggest that some caution must be used in inferring structural relationships established on the basis of assembly deposition sequences, particularly when neutral surfactants are used as film components.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM15,238) for support of this work and to Mrs. Marjorie Richter for technical assistance.

References and Notes

(1) Photochemical Reactivity in Organized Assemblies 15. Part 14: Whitten, D. G.; DeLaive, P. J.; Foreman, T. K.; Mercer-Smith, J. A.; Schmehl, R. H.; Giannotti, C. In "Solar Energy, Chemical Conversion and Storage", King, R. B., Kutal, C. R., Hautala, R. R., Ed.; Humana Press: Clifton, N.J., 1979; p 117.

(2) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems", Academic Press: New York, 1975.

(3) Hartley, G. S. *Trans Faraday Soc.* **1934**, *30*, 444.

(4) Dunlap, R. B.; Cordes, E. H. *J. Phys. Chem.* **1969**, *73*, 361.

(5) Bunton, C. A.; Robinson, L.; Schaak, J.; Stam, M. F. *J. Org. Chem.* **1971**, *36*, 2346.

(6) Kogl, F.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1940**, *59*, 600.

(7) Fosbinder, R. J.; Rideal, E. K. *Proc. R. Soc. London, Ser. A* **1933**, 143.

(8) Gee, G.; Rideal, E. K. *Proc. R. Soc. London, Ser. A* **1935**, *153*, 116.

(9) Gaines, G. L., Jr. "Insoluble Monolayers at Liquid-Gas Interfaces", Wiley-Interscience: New York, 1966.

(10) Hopf, F. R.; Mobius, D.; Whitten, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 1584.

(11) Turro, N. J.; Liu, K.-C.; Chow, M.-F. *Photochem. Photobiol.* **1977**, *26*, 413.

(12) Valenty, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1.

(13) Worsham, P. R.; Eaker, D. W.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 7091.

(14) Schmehl, R. H.; Shaw, G. L.; Whitten, D. G. *Chem. Phys. Lett.* **1978**, *58*, 549.

(15) Whitten, D. G.; Eaker, D. W.; Horsey, B. E.; Schmehl, R. H.; Worsham, P. R. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 858.

(16) Hopf, F. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 7422.

(17) Geiger, M. W.; Turro, N. J. *Photochem. Photobiol.* **1976**, *26*, 22.

(18) Turro, N. J.; Kraeutler, B. *J. Am. Chem. Soc.* **1978**, *100*, 7432.

(19) Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7431.

(20) Fuhrhop, J.-H.; Lumbantobing, T. *Tetrahedron Lett.* **1970**, 2815.

(21) Harel, Y.; Manassen, J. *J. Am. Chem. Soc.* **1977**, *99*, 5817.

(22) Whitten, D. G.; Yau, J. C.; Carroll, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 2291.

(23) Whitten, D. G.; Yau, J. C. *Tetrahedron Lett.* **1969**, 3077.

(24) Seely, G. R.; Calvin, M. *J. Chem. Phys.* **1955**, *23*, 1068.

(25) Suboch, W. P.; Losev, A. P.; Gurinovitch, G. P. *Photochem. Photobiol.* **1974**, *20*, 183.

(26) Seely, G. R.; Talmadge, K. *Photochem. Photobiol.* **1964**, *3*, 195.

(27) Mercer-Smith, J. A.; Sutcliffe, C. R.; Schmehl, R. H.; Whitten, D. G., *J. Am. Chem. Soc.* **1979**, *101*, 3995.

(28) Reference 9, p 162.

(29) Kuhn, H.; Mobius, D.; Bucher, H. "Physical Methods of Chemistry", Vol. I; Part 3B; Weissburger, A., Rossiter, B., Eds.; Wiley: New York, 1972; p 588.

(30) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513.

(31) Brockway, L. O.; Karle, J. *J. Colloid Sci.* **1947**, *2*, 277.

(32) Bigelow, W. C.; Brockway, L. O. *J. Colloid Sci.* **1956**, *11*, 60.

(33) Bartell, L. S.; Ruch, R. J. *J. Phys. Chem.* **1956**, *60*, 123. **1959**, *63*, 1045.

(34) Takenaka, T.; Nogami, K.; Gotch, H.; Gotch, R. *J. Colloid Interface Sci.* **1971**, *35*, 395.

(35) Horsey, B. E.; Hopf, F. R.; Schmehl, R. H.; Whitten, D. G. "Porphyrin Symp., Adv."; Longo, F. R., Ed.; Ann Arbor Science: Ann Arbor, Mich., 1979; p 17.

(36) Horsey, B. E.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 1293.

(37) Kuhn, H.; Mobius, D. *Angew Chem., Int. Ed. Engl.* **1971**, *10*, 620.

(38) Bruning, R. Dissertation, University of Marburg, 1969.

(39) Polymeropoulos, E. E.; Sagiv, J. *J. Chem. Phys.* **1978**, *69*, 1836.

(40) Richard, M. A.; Deutch, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 6613.

(41) Hopf, F. R. Ph.D. Thesis, University of North Carolina, 1974.

(42) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427.

(43) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

(44) O'Rourke, M.; Curran, C. *J. Am. Chem. Soc.* **1970**, *92*, 1501.

(45) Eisner, U.; Harding, M. J. C. *J. Am. Chem. Soc.* **1964**, *86*, 4089.

(46) Fromherz, P. *Rev. Sci. Instrum.* **1975**, *46*, 1380.

(47) Mercer-Smith, J. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 2620.

(48) In the case of irradiation of SnPF,THA(Cl)$_2$ with water present but no added reductant a slow buildup of product having absorption at 620 nm (chlorin region) was observed. The rate of product formation was less than one-half that produced with aqueous $SnCl_2$ and about 10% of that observed with added DMA.

(49) In studies where samples containing several layers of porphyrins were compared with those containing only a few, the total number of slides in each set was adjusted so that total light absorption was the same as in each system.

(50) Eastwood, D.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *35*, 359.

(51) Callis, J. B.; Gouterman, M.; Jones, Y. M.; Henderson, B. H. *J. Mol. Spectrosc.* **1971**, *39*, 410.

(52) Gouterman, M. In "The Porphyrins", Vol. III; Dolphin, D., Ed.; Academic Press: New York, 1978; p 1.

(53) Mercer-Smith, J. A., unpublished results.

(54) Whitten, D. G.; Mercer-Smith, J. A.; Schmehl, R. H.; Worsham, P. R. *Adv. Chem. Ser.*, in press.

(55) Costa, S. M. B.; Macanita, A. L. *J. Photochem.* **1978**, *9*, 295. Manuscript in press. We thank Dr. Costa for a preprint of this work.

(56) Seefeld, K. P.; Mobius, D.; Kuhn, H. *Helv. Chim. Acta* **1977**, *60*, 2608.

(57) Kuhn, H. *Pure Appl. Chem.*, **1979**, *51*, 341.