Photoionization of (*p*-Alkylphenyl)triphenylporphyrins in Neutral and Positively and Negatively Charged Vesicles: Effects of Alkyl Chain Length and Addition of Chloroalkanes

Hyung Mi Sung-Suh and Larry Kevan*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Received: July 8, 1996; In Final Form: November 19, 1996[⊗]

The photoionization of (*p*-alkylphenyl)triphenylporphyrins (C_nPtPP) in cationic dioctadecyldimethylammonium chloride (DODAC), neutral dipalmitoylphosphatidylcholine (DPPC), and anionic dihexadecyl phosphate (DHP) frozen vesicles has been studied by electron spin resonance (ESR) with visible light irradiation at 77 K with and without addition of chloroalkanes (CCl_4, $CHCl_3$, CH_2Cl_2, or $CH_3CH_2CH_2Cl$) as electron acceptors. C_nPtPP ($n = 3$, 6, 9, and 12) were synthesized and used to study the effects of alkyl chain length. The photoionization efficiency was found to decrease with increasing alkyl chain length of C_nPtPP. The relative photoyield of the porphyrin cation radical (C_nPtPP^+) measured by ESR decreased in the order DODAC > DPPC > DHP. The addition of CCl_4, $CHCl_3$, CH_2Cl_2, or $CH_3CH_2CH_2Cl$ into C_9PtPP/DHP vesicles enhanced the C_9PtPP^+ radical photoyield. All four chloroalkanes acted as better electron acceptors in competition with water at the vesicle interface. The results are discussed in terms of the alkyl chain length of C_nPtPP, the vesicle surface charge, and the effects of chloroalkanes as electron acceptors.

Introduction

Photochemical solar energy conversion is a vitally important and active research area because visible light is an inexpensive and ever renewable source of energy.[1−3] Photoinduced charge separation of photoionizable molecules in heterogeneous systems such as vesicles, micelles, and porous inorganic materials has been studied with a goal to design artificial photoredox systems for solar energy conversion and storage.[3−18] So, it is important to study the photoionization of molecules photoionized with visible light. For this purpose, porphyrin derivatives have been used as photosensitive electron donors due to their structural and functional similarities to chlorophylls and their absorption of visible light.[6−9]

In order to achieve light energy utilization in molecular assemblies such as micelles, vesicles, and reverse micelles, it is necessary to control the net charge separation efficiency to minimize the back electron transfer.[3−5,8−18] This net charge separation efficiency is strongly affected by structural factors such as the surface charge distribution of the vesicles, the degree of interaction between water and the surface of the molecular assembly, and the location of the electron donors and acceptors. It has been shown that these structural factors are controllable by changing the counterion, surfactant headgroup, and alkyl chain length of the photoionizable donors and adding salts or electron acceptors. The yield of photoinduced cation radical or converted paramagnetic products can be measured in the frozen state with electron spin resonance (ESR). In previous work, the location of photoionizable molecules such as alkylviologen,[11] alkylphenothiazine,[13−16] or (*p*-alkoxyphenyl)triphenylporphyrin[17,18] within vesicles or micelles was controlled by varying the pendant alkyl chain length. By altering the alkyl chain length, one can change the hydrophobicity of the photoionizable molecules. The location of the photoionizable molecule relative to a surfactant assembly interface can be determined by the deuterium modulation depth of electron spin echo modulation (ESEM) of the photoinduced cation radical in surfactant assemblies in deuterated water.[11−18]

Halogenated compounds have been used as electron acceptors or excited state quenchers in flash photolysis studies of aromatic compounds such as pyrene,[19] *N*,*N*,*N*′,*N*′-Tetramethylbenzidine (TMB),[20,21] and *N*,*N*,*N*′,*N*′-tetramethylphenylenediamine (TMPD).[22] Also, the chloromethanes (CCl_4, $CHCl_3$, CH_2Cl_2, or CH_3Cl) were studied as electron acceptors for the photoionization of phenothiazine in silica gels.[23] Those results showed CCl_4 and $CHCl_3$ to act as more efficient electron acceptors than CH_2Cl_2 and CH_3Cl and also that CH_2Cl_2 and CH_3Cl are less efficient electron acceptors in comparison with the silica gel framework so that there is no enhancement of the photoyield with CH_2Cl_2 or CH_3Cl in silica gels.

In this present study, (*p*-alkylphenyl)triphenylporphyrins (C_nPtPP, $n = 3$, 6, 9, 12) as photoionizable molecules were synthesized, and their photoionization with visible light was investigated in cationic dioctadecyldimethylammonium chloride (DODAC), neutral dipalmitoylphosphatidylcholine (DPPC), and anionic dihexadecyl phosphate (DHP) frozen vesicles at 77 K with and without addition of chloroalkanes (CCl_4, $CHCl_3$, CH_2Cl_2, or $CH_3CH_2CH_2Cl$) as electron acceptors. The yield of the photoinduced porphyrin cation radical (C_nPtPP^+) was measured by ESR at 77 K. It was found that the C_nPtPP^+ photoyield is affected by the alkyl chain length of C_nPtPP and the interface charge type of the vesicle. Also, the photoyield was much enhanced by the addition of chloroalkanes as electron acceptors. Each chloroalkane (CCl_4, $CHCl_3$, CH_2Cl_2, and $CH_3CH_2CH_2Cl$) acts as a better electron acceptor in comparison to water at the vesicle interface.

Experimental Section

Materials. The (*p*-alkylphenyl)triphenylporphyrins (C_nPtPP, $n = 3$, 6, 9, and 12) were synthesized from *p*-alkylbenzaldehydes (C_nPCOH), benzaldehyde, and pyrrole. *p*-Alkylbenzaldehydes with $n = 3$, 6 , 9, and 12 were also prepared from *p*-alkylbenzene, hexamethylenetetramine, and CF_3COOH. Benzaldehyde, *p*-alkylbenzenes ($n = 3$, 6, 9, and 12), pyrrole, propionic acid, hexamethylenetetramine, CF_3COOH , and $CDCl_3$ were purchased from Aldrich. Ether, chloroform (HPLC grade), and hexane (HPLC grade) were purchased from Mallinckrodt. All chemicals were used without further purification, except pyrrole which was freshly distilled. Gravity column chromatography was performed on silica gel 62 (60−200 mesh) from Mallinckrodt.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S1089-5639(96)02001-4 CCC: $14.00

^{1}H NMR spectra at 300 MHz were recorded on a General Electric QE-300 spectrometer at room temperature in $CDCl_3$ solution. UV−vis absorption spectra were obtained on a Perkin-Elmer Model 330 spectrophotometer with a 1 cm path length quartz cell.

DHP and DPPC were obtained from Sigma Chemical Co. and used without further purification. DODAC was prepared from dioctadecyldimethylammonium bromide (DODAB) purchased from Eastman Kodak and purified by recrystallization in acetone. A methanol/chloroform (70:30 v/v) solution of DODAB was passed through a chloride ion exchange resin type AG 2 × 8, 20−50 mesh, from Biorad Laboratory, to form DODAC. The eluent containing DODAC was evaporated, and the solid residue was recrystallized two times from acetone/water (95:5 v/v). Tris(hydroxymethyl)aminomethane (Tris, Gold Label, 99.9+%) and 2 N hydrochloric acid were purchased from Aldrich and Sigma Chemical Co., respectively.

C_nPCOH. *p*-Alkybenzaldehydes (C_nPCOH, $n = 3$, 6, 9, and 12) were synthesized using the procedure by Nakai.[24] A mixture of *p*-alkylbenzene (50 mmol) and hexamethylenetetramine (55 mmol) in CF_3COOH (50 mL) was refluxed at 80 °C overnight. After cooling, the mixture was concentrated under reduced pressure, made alkaline with aqueous $NaHCO_3$, and extracted with ether. The extract was washed, dried, and concentrated to give C_nPCOH as an oil. The amount of C_nPCOH obtained was 35 mmol with a 70% yield. ^{1}H NMR ($CDCl_3$): δ 10.0 (s, 1 H −COH), 8.53 (d, 2 H, *2*,*6*-phenyl protons), 7.65 (d, 2 H, *3*,*5*-phenyl protons), 2.73 (t, 2 H, benzyl protons), 0.95 (t, 3 H, $-CH_3$) ppm.

C_nPTPP. A mixture of C_nPCOH (35 mmol) and benzaldehyde (105 mmol) was added dropwise to 400 mL of refluxing propionic acid, followed by freshly distilled pyrrole (140 mmol). After refluxing with stirring for 1.5 h, the reaction mixture was distilled to remove propionic acid and concentrated until the purple solid is left. This purple solid is the crude product which contains *meso*-tetraphenylporphyrin, C_nPtPP, and other byproduct alkylporphyrins. C_nPtPP was isolated and purified by using gravity column chromatography. The crude product was chromatographed on a silica gel column once with chloroform as eluent and then two times with chloroform−hexane (3:7 v/v). The final purification by recrystallization in chloroform−methanol led to a pure purple crystal of C_nPtPP.

C_3PtPP: Yield 1.3%; ^{1}H NMR ($CDCl_3$) δ 8.86 (m, 8 H, π-pyrrole), 8.32 (m, 6 H, *m*-phenyl protons), 8.12 (d, 2 H, *2*,*6*-phenyl protons), 7.76 (m, 9 H, *o*- and *p*-phenyl protons), 7.55 (d, 2 H, *3*,*5*-phenyl protons), 2.95 (t, 2 H, benzyl protons), 1.96 (m, 2H, $-CH_2-$), 1.20 (t, 3 H, $-CH_3$), −2.75 (s, 2 H, 2 NH) ppm.

C_6PtPP: Yield 1.7%; ^{1}H NMR ($CDCl_3$) δ 8.84 (m, 8 H, π-pyrrole), 8.32 (m, 6 H, *m*-phenyl protons), 8.12 (d, 2 H, *2*,*6*-phenyl protons), 7.76 (m, 9 H, *o*- and *p*-phenyl protons), 7.55 (d, 2 H, *3*,*5*-phenyl protons), 2.95 (t, 2 H, benzyl protons), 1.32−1.83 (m, 8 H, $-(CH_2)_4-$), 1.05 (t, 3 H, $-CH_3$), −2.77 (s, 2 H, 2 NH) ppm.

C_9PtPP: Yield 2.0%; ^{1}H NMR ($CDCl_3$) δ 8.83 (m, 8 H, π-pyrrole), 8.32 (m, 6 H, *m*-phenyl protons), 8.12 (d, 2 H, *2*,*6*-phenyl protons), 7.76 (m, 9 H, *o*- and *p*-phenyl protons), 7.55 (d, 2 H, *3*,*5*-phenyl protons), 2.95 (t, 2 H, benzyl protons), 1.30−1.70 (m, 8 H, $-(CH_2)_7-$), 0.95 (t, 3H, $-CH_3$), −2.79 (s, 2 H, 2 NH) ppm.

$C_{12}PtPP$: Yield 2.5%; ^{1}H NMR ($CDCl_3$) δ 8.82 (m, 8 H, π-pyrrole), 8.32 (m, 6 H, *m*-phenyl protons), 8.12 (d, 2 H, *2*,*6*-phenyl protons), 7.76 (m, 9 H, *o*- and *p*-phenyl protons), 7.55 (d, 2 H, *3*,*5*-phenyl protons), 2.95 (t, 2 H, benzyl protons), 1.32−1.62 (m, 8 H,$-(CH_2)_{10}-$), 0.91 (t, 3 H, $-CH_3$), −2.85 (s, 2 H, 2 NH) ppm.

Vesicle Preparation. Stock solutions of C_nPtPP and of the surfactant (DODAC, DPPC, DHP) were prepared in chloroform with concentrations of 10 and 20 mM, respectively. For the preparation of DODAC or DPPC vesicle solution containing C_nPtPP, 40 μL of C_nPtPP stock solution and 1 mL of DODAC or DPPC stock solution were transferred into a 16 × 125 mm Fisher test tube. The chloroform was evaporated by flowing nitrogen gas over the surface of solution in the test tube to form a thin film of C_nPtPP and surfactant on the test tube wall. After the film had formed, 1 mL of deionized water was added, and then the resulting solution was sonicated at 55 ± 3 °C under nitrogen gas for 30 min or until the solution was clear. For the preparation of DHP vesicle solution, 1 mL of a 20 mM of Tris buffered solution adjusted to pH = 7.8 with hydrochloric acid was added to a thin film of C_nPtPP and DHP in the test tube. The solution was then sonicated at 70 ± 3 °C under nitrogen gas. The concentration of each C_nPtPP in the vesicle solution was determined to be 1.8×10^{-4} M by UV−vis absorption spectra ($\lambda_{max} = 516$ nm in chloroform, $\epsilon = 1.8 \times 10^3$ M^{-1} cm^{-1}).

For the preparation of C_9PtPP in DHP vesicles with chloroalkanes (C_9PtPP/chloroalkane/DHP = 0.4/8/20 mM), the calculated amount of chloroalkane was injected into the C_9PtPP in DHP vesicle solution with a micropipet after sonication and shaken vigorously.

Then 100 μL of each vesicle solution was transferred into 2 mm i.d. × 3 mm o.d. Suprasil quartz tubes which were sealed at one end. The sample tubes were frozen rapidly at 77 K by plunging them into liquid nitrogen.

Photoirradiation and ESR. Photoirradiation for ESR measurement was carried out at 77 K with a 300 W Cermax xenon lamp (ILC-LX 300 UV). The light was passed through a 10 cm water filter and a Corning No. 0-56 glass filter which passes light of wavelength longer than 300 nm. The samples were irradiated in liquid nitrogen in a quartz Dewar that was rotated at 4 rpm to ensure even irradiation of the samples. The light intensity at the sample position was measured with a YSI-Kettering Model 65 radiometer as $1.0 \times 10^{\ 3}$ W m^2. ESR spectra were recorded at 77 K at X-band using a Bruker ESP 300 spectrometer with 100 kHz field modulation and 0.5 mW microwave power to avoid power saturation. The photoinduced radical yield was determined by double integration of the ESR spectra using the ESP 300 software. Each relative photoyield value is an average of triple determinations.

Results

The structures of the molecules used in this study are shown in Figure 1. The vesicle samples without C_nPtPP did not show any ESR signal. This indicates that C_nPtPP is the only photoionizable molecule in the system. The photoinduced C_nPtPP^+ radical yield was obtained from double integration of the ESR spectrum after 30 min photoirradiation with $\lambda > 300$ nm at 77 K. The porphyrin photoionization process is believed to be a two-photon process via the triplet state by analogy to chlorophyll in frozen solutions of vesicles.[25] Absolute quantum yields are not measured in the frozen solutions due to the extensive light scattering which makes the determination of the absorbed quanta uncertain. So the results are discussed in terms of relative photoyield trends.

Photoionization without Chloroalkanes. Figures 2 and 3 show the ESR spectra from the photoinduced C_nPtPP^+ radical in the frozen vesicles of DODAC, DPPC , and DHP after 30 min photoirradiation ($\lambda > 300$ nm) at 77 K. The color of each sample turns from brown to green with photoirradiation. The ESR signal from each photoirradiated sample shows a singlet at $g = 2.0025$ with a line width of 7 G, which is assigned to

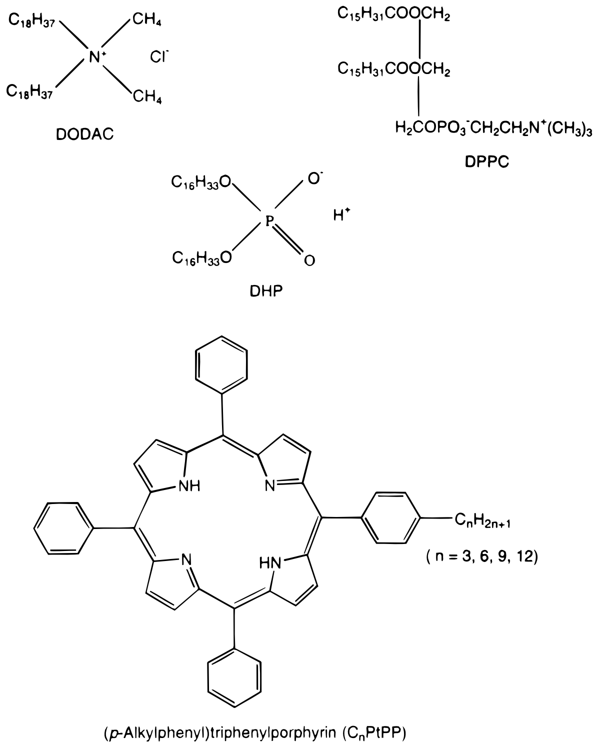

Figure 1. Structures of surfactants and (*p*-alkylphenyl)triphenylporphyrins (C_nPtPP) used in this study.

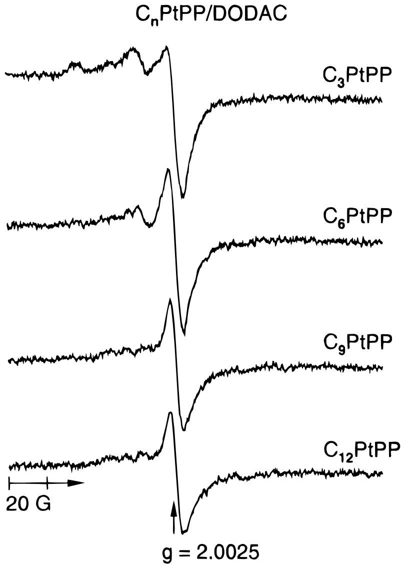

Figure 2. ESR signals of C_nPtPP$^+$ radical photoinduced at 77 K in DODAC vesicles after 30 min photoirradiation with $\lambda > 300$ nm at 77 K.

the photoinduced C_nPtPP$^+$ radical, and a background multiplet, which is an octet with a 22 mT coupling previously assigned[11-18] to a secondary alkyl radical formed by photoinduced radical conversion from C_nPtPP$^+$ radical to the alkyl chain of the surfactants. This multiplet of the secondary alkyl radical was already reported in vesicles and micelles with other photoionizable molecules such as alkylviologen,[11] alkylphenothiazine,[13-16] and (*p*-alkoxyphenyl)triphenylporphyrin.[17,18] This alkyl radical is not observed from the frozen vesicle without C_nPtPP after photoirradiation. The ESR signal of the secondary alkyl radical is more clearly resolved into an octet with about 22 mT coupling in the intense ESR signal from C_nPtPP$^+$/CCl_4/DHP as shown in Figure 5. Figure 4 shows the normalized photoyield of C_nPtPP$^+$ radical in DODAC, DPPC, and DHP vesicles after 30 min photoirradiation ($\lambda > 300$ nm) at 77 K. The C_nPtPP$^+$ radical photoyield and the ESR signal intensity of the secondary alkyl radical decrease in the order DODAC > DPPC > DHP. Also, the C_nPtPP$^+$ radical ion photoyield decreases with increasing alkyl chain length of C_nPtPP. The intensity of the ESR signal from the secondary alkyl radical decreases with increasing alkyl chain length of C_nPtPP.

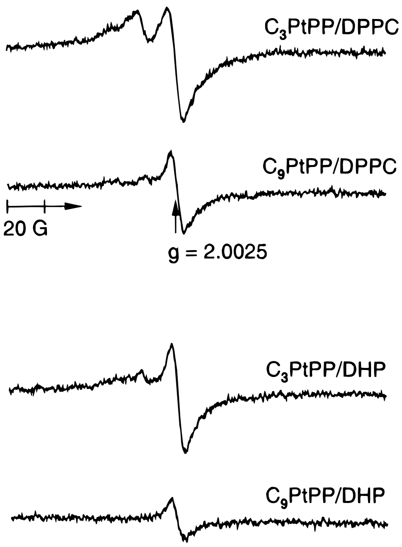

Figure 3. ESR signals of C_3PtPP$^+$ and C_9PtPP$^+$ radicals in DPPC and DHP vesicles after 30 min photoirradiation with $\lambda > 300$ nm at 77 K.

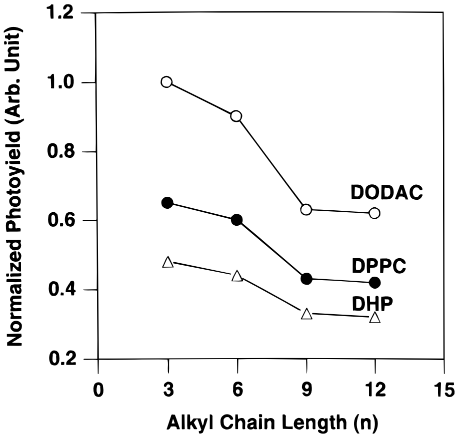

Figure 4. Normalized photoyields of C_nPtPP$^+$ radicals in DODAC (m), DPPC (l), and DHP (Δ) vesicles versus the alkyl chain length (C_n) of C_nPtPP after 30 min photoirradiation with $\lambda > 300$ nm at 77 K.

Photoionization with Chloroalkanes. Figure 5 shows ESR signals from C_9PtPP$^+$ in DHP vesicle with CCl_4, $CHCl_3$, CH_2Cl_2, or $CH_3CH_2CH_2Cl$ as an electron acceptor after 30 min photoirradiation ($\lambda > 300$ nm) at 77 K. The concentration of C_9PtPP, chloroalkane, and DHP was 0.4, 8, and 20 mM, respectively. The photoirradiated sample showed a more intense green color compared to the sample of C_nPtPP in vesicles without chloroalkanes. Before photoirradiation, there is no ESR signal from this sample. Also, no ESR signal is observed from a photoirradiated sample of only the chloroalkane in DHP vesicles without C_9PtPP. The ESR signal from each sample shows a singlet from the C_9PtPP$^+$ radical and a multiplet from a secondary alkyl radical from the DHP alkyl chain formed by radical conversion as mentioned above. No ESR signals from other radicals such as $CHCl_3^-$, $^\bullet CHCl_2$, $^\bullet CCl_4^-$, or $^\bullet CCl_3$ generated from chloroalkanes are observed from these samples after photoirradiation at 77 K. The C_9PtPP$^+$ radical photoyield increases by increasing the ratio of C_9PtPP to chloroalkane in DHP vesicles to about 20.

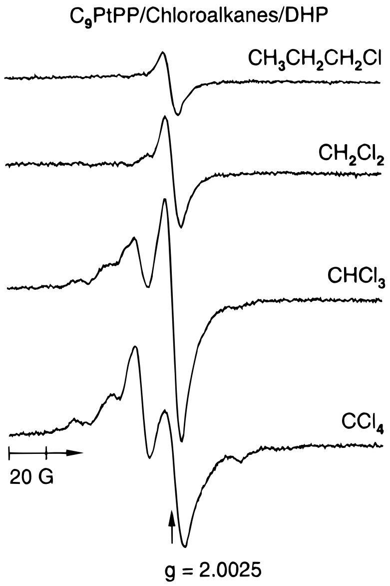

Figure 5. ESR signals of C_9PtPP^+ radicals in DHP vesicles with addition of CCl_4, $CHCl_3$, CH_2Cl_2, or $CH_3(CH_2)_2Cl$ as electron acceptors after 30 min photoirradiation with $\lambda > 300$ nm at 77 K. (C_9PtPP/chloroalkane/DHP = 0.4/8/20 mM).

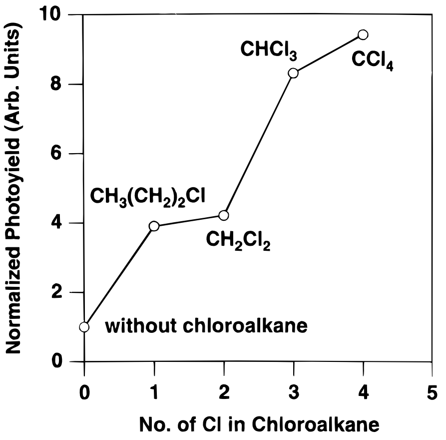

Figure 6. Normalized photoyield of C_9PtPP^+ radical in DHP vesicles with added CCl_4, $CHCl_3$, CH_2Cl_2, and $CH_3(CH_2)_2Cl$ after 30 min photoirradiation with $\lambda > 300$ nm at 77 K.

As shown in Figure 6, the addition of CH_3Cl or $CH_3(CH_2)_2$-Cl to C_9PtPP in DHP vesicles increases the C_9PtPP^+ radical photoyield about 4 times compared to that of a sample of only C_9PtPP in DHP vesicles. Also, the photoyield of C_9PtPP^+ in DHP vesicles with CCl_4 or $CHCl_3$ is about 9 times larger than that of C_9PtPP^+ in DHP without CCl_4 or $CHCl_3$. And a sample with CCl_4 or $CHCl_3$ shows a much more intense green color than other samples after photoirradiation. A more intense ESR signal from secondary alkyl radicals is also observed from C_9PtPP^+ in DHP vesicles with chloroalkane than from a sample without chloroalkane. The ESR signal from the secondary alkyl radical is more intense and better resolved in a sample with CCl_4 or $CHCl_3$ than in a sample with CH_2Cl_2 or $CH_3(CH_2)_2Cl$. This result shows that the C_9PtPP^+ radical photoyield decreases in the order $CCl_4 > CHCl_3 > CH_2Cl > CH_3(CH_2)_2Cl$. The intensity of ESR signal from the secondary alkyl radical also decreases in the same order.

Discussion

The singlet ESR signal of the C_nPtPP^+ radical shows $g = 2.0025$, which is consistent with the g values of porphyrin derivatives reported previously.[6−10,17,26] The multiplet ESR signal measured along with the singlet of C_nPtPP^+ radical is assigned to the secondary alkyl radical formed by a photoinduced radical conversion from C_nPtPP^+ radical to the alkyl chain of the surfactant, which was already assigned in previous studies for alkylviologen,[11] alkylphenothiazine,[13−16] or (*p*-alkoxyphenyl)triphenylporphyrin[17,18] in the same vesicles. The results from the photoionization of alkylviologen (AV^{2+}) in the vesicles indicates the radical conversion from the AV^+ radical to the surfactant alkyl chain is induced by photoirradiation with light in the range $240 < \lambda < 300$ nm, and this alkyl radical is not observed with $\lambda > 300$ nm. Also, for AV^{2+} in vesicles, the alkyl radical is observed in DODAC and DPPC, but not in DHP vesicles. But, in the present experiment with C_nPtPP^+ in vesicles, such a radical conversion is induced by photoirradiation even with $\lambda > 300$ nm, and the secondary alkyl radical is observed in all three vesicles, DODAC, DPPC, and DHP, in contrast to the results for AV^{2+} in vesicles. The relative intensities of this alkyl radical decreases in the order DODAC > DPPC > DHP and also decreases with an increase in the alkyl chain length of C_nPtPP. This result indicates that for C_nPtPP in vesicles the energy of the light with $\lambda > 300$ nm is sufficient to induce a conversion from the C_nPtPP^+ radical to a surfactant alkyl chain radical. The ESR intensity of the alkyl radical changes in parallel with the photoyield change; this indicates that the relative rate of photoinduced radical conversion seems to be proportional to the concentration of C_nPtPP^+ radicals.

Effect of Alkyl Chain Length of C_nPtPP. The relative distance from the C_nPtPP^+ moiety to the bulk interface water which acts as an electron acceptor in vesicle systems is a critical factor for efficient photoinduced electron transfer from C_nPtPP^+ as previously reported in the same vesicle systems.[5,8−18] A shorter distance from the C_nPtPP^+ moiety to the interface water provides more efficient electron transfer and gives a higher C_nPtPP^+ radical yield. The photoyield calculated from the double integration of the ESR signal indicates the efficiency of photoinduced electron transfer. As shown in Figure 4, a decrease in photoyield with increasing alkyl chain length of C_nPtPP is interpreted as an increase in the relative distance for electron transfer from C_nPtPP to interface water of the vesicle system. This can be explained by an increase in the hydrophobic interaction between the C_nPtPP alkyl chain and the surfactant alkyl chain as the alkyl chain length of C_nPtPP increases.

Previously, the relative distance changes with alkyl chain length for alkylphenothiazines,[13−18] alkylviologens,[11] and (*p*-alkoxyphenyl)triphenylporphyrins[17] in the same vesicles were monitored by the deuterium modulation depth in electron spin echo modulation (ESEM) studies.[27] The results of these previous ESEM studies show that the greater hydrophobic interaction locates the photoionizable molecules deeper into the hydrocarbon region of the vesicle and provides a longer distance for electron transfer from the photoionizable molecules to interface water, which results in a decrease in the efficiency of photoinduced electron transfer. The same alkyl chain length effect for C_nPtPP on the efficiency of electron transfer is supported by these previous ESEM experiments. The ESR signals from C_nPtPP^+ were too weak to carry out reliable ESEM experiments.

Effect of Interface Charge and Interface Order. As shown in Figure 4, the photoyields decrease in the order DODAC > DPPC > DHP. Consequently, photoinduced electron transfer through cationic DODAC vesicles shows the best photoyield. This result can be explained by the interface charge and the interface order of the vesicles. The photoyields are affected by the strength and kind of interface charge of the vesicles which varies the barrier for electron penetration through the vesicle interface as reported before.[11−18] An anionic interface charge of DHP vesicles constitutes a higher energy barrier for electron

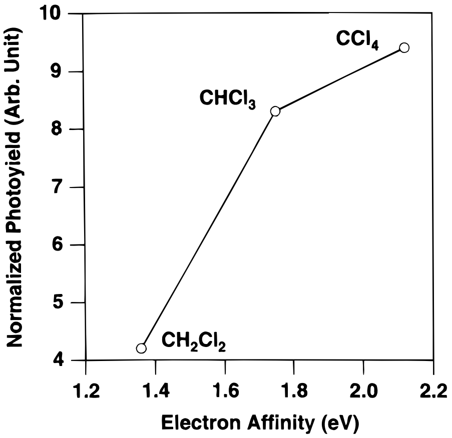

Figure 7. Normalized photoyield of C_9PtPP^+ radical in DHP vesicles with added CCl_4, $CHCl_3$, CH_2Cl_2 versus the electron affinities (eV) of the chloroalkanes after 30 min photoirradiation with $\lambda > 300$ nm at 77 K.

transfer across the interface than a cationic charge of DODAC or a neutral charge of DPPC vesicles.

The less ordered interface region of DODAC vesicles due to the bulky dimethylammonium headgroup allows greater penetration of the porphyrin molecule into the hydrocarbon region of the vesicle compared to that in DPPC and DHP vesicles which have better oriented interfaces. This means that the distance for electron transfer from porphyrin to interface water increases as DODAC > DPPC > DHP, which has been verified by the deuterium modulation depth in ESEM experiments for alkylphenothiazines,[13-16] alkylviologens,[11] and (*p*-alkoxyphenyl)triphenylporphyrins[17] in the same vesicles. But, even with a shorter distance for electron transfer in anionic DHP vesicles, the photoyield is lower than in cationic DODAC and in neutral DPPC vesicles. This indicates that the vesicle surface charge effect dominates the small distance difference.

Effect of Chloroalkanes as Electron Acceptors. As shown in Figures 5 and 6, the photoyield of C_9PtPP^+ in DHP vesicles is enhanced by the addition of CCl_4, $CHCl_3$, CH_2Cl_2, or $CH_3CH_2CH_2Cl$ as electron acceptors. This result indicates that these four chloroalkanes act as better electron acceptors than water at the vesicle interface. In a previous study of the photoionization of phenothiazine in silica gels,[23] only $CHCl_3$ and CCl_4 enhanced the photoyield. But in our experiments, CH_2Cl_2 and $CH_3Cl_2CH_2Cl$ also enhance the photoyield. The enhancement of the C_nPtPP^+ radical photoyield increases with the number of Cl atoms in the chloroalkanes in the order $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3CH_2CH_2Cl$. This result can be explained by the different electron affinities of chloroalkanes (2.12, 1.75, and 1.36 eV for CCl_4, $CHCl_3$, and CH_2Cl_2, respectively).[19-23,28] Photoinduced electron transfer is achieved via quenching a photoexcited state-of-the-art electron donor by the electron acceptor. It has been reported that the quenching rate is related to the electron affinity of the electron acceptor or quencher for a variety of systems including UV-excited aromatics by chloromethane and that the quantum yield or photoyield is proportional to the quenching rate.[19-22] Those experimental data show a qualitative increase of the quenching rate with a decreasing difference of the ionization potential of the host or electron donor minus the electron affinity of the quencher or electron acceptor. In our experiment with C_9PtPP/chloroalkane/DHP vesicle, C_9PtPP is used as an electron donor for all samples, so the quenching rate should be related only to the electron affinities of the chloroalkanes as is shown in Figure 7. The result shows that the photoyield of C_nPtPP^+ in DHP vesicles with the addition of chloroalkanes is proportional to the gas phase electron affinities of the chloroalkanes. Electron transfer from C_nPtPP to CCl_4 or $CHCl_3$ may produce radicals such as CCl_4^-, $CHCl_3^-$, or $^\bullet CCl_3$,[19-23] but these do not seem to be stable enough to be detected.

Conclusions

The photoyield of the C_nPtPP^+ radical in vesicles induced by photoirradiation with the light ($\lambda > 300$ nm) at 77 K increases in the order cationic DODAC > neutral DPPC > anionic DHP, which indicates that the efficiency of electron transfer through the vesicle surface strongly depends on the vesicle interface charge. A decrease in photoyield with increasing alkyl chain length of C_nPtPP is due to an increasing hydrophobic interaction between the C_nPtPP alkyl chain and the surfactant alkyl chain of the vesicles with increasing alkyl chain length of C_nPtPP which locates the porphyrin moiety deeper into the hydrocarbon region of the vesicles. Radical conversion from the C_nPtPP^+ radical to the surfactant alkyl chain is induced by photoirradiation even with $\lambda > 300$ nm. The addition of CCl_4, $CHCl_3$, CH_2Cl_2, or $CH_3(CH_2)_2Cl$ into C_9PtPP in DHP vesicles enhances the photoyield of the C_9PtPP^+ radical. All four chloroalkanes act as better electron acceptors than water at the vesicle interface. The enhancement of the photoyield by chloroalkanes depends on their electron affinities, and the photoyield decreases in the order $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3(CH_2)_2Cl >$ no chloroalkane.

Acknowledgment. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Science, Office of Energy Research, U.S. Department of Energy and by the University of Houston Energy Lab.

References and Notes

(1) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic: New York, 1987.
(2) Fendler, J. H. *Acc. Chem. Res.* **1980**, *13*, 7.
(3) Connolly, J. S., Ed. *Photochemical Conversion and Storage of Solar Energy*; Academic: New York, 1981.
(4) Kevan, L. In *Photoinduced Electron Transfer, Part B*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; pp 329 −384.
(5) Kevan, L. *Int. Rev. Phys. Chem.* **1990**, *9*, 807.
(6) Rotenberg, M.; Margalit, R. *Biochem. Biophys. Acta* **1987**, *905*, 173.
(7) Groves, J. T.; Newman, R. *J. Am. Chem. Soc.* **1989**, *111*, 2900.
(8) Lanot, M. P.; Kevan, L. *J. Phys. Chem.* **1989**, *93*, 998.
(9) Chastenet de Castaing, E.; Kevan, L. *J. Phys. Chem.* **1991**, *95*, 10178.
(10) Lanot, M. P.; Kevan, L. *J. Phys. Chem.* **1991**, *95*, 6399.
(11) Sakaguchi, M.; Kevan, L. *J. Phys. Chem.* **1989**, *93*, 6039.
(12) Lanot, M. P.; Kevan, L. *J. Phys. Chem.* **1989**, *93*, 5280.
(13) Kang, Y. S.; McManus, H. J. D.; Kevan, L. *J. Phys. Chem.* **1992**, *96*, 10049.
(14) Kang, Y. S.; McManus, H. J. D.; Kevan, L. *J. Phys. Chem.* **1992**, *96*, 10055.
(15) Kang, Y. S.; McManus, H. J. D.; Kevan, L. *J. Phys. Chem.* **1992**, *96*, 7473.
(16) Kang, Y. S.; McManus, H. J. D.; Kevan, L. *J. Phys. Chem.* **1993**, *97*, 2027.
(17) Kang, Y. S.; McManus, H. J. D.; Kevan, L. *J. Phys. Chem.* **1994**, *98*, 4389.
(18) Kang, Y. S.; McManus, H. J. D.; Kevan, L. *J. Phys. Chem.* **1994**, *98*, 1044.
(19) Piciulo, P. L.; Thomas, J. K. *J. Phys. Chem.* **1978**, *68*, 3260.
(20) Alford, P. C.; Cureton, C. G.; Lampert, R. A.; Phillips, D. *Chem. Phys.* **1983**, *76*, 103.
(21) Shimamori, H.; Tatsumi, Y. *J. Phys. Chem.* **1993**, *97*, 9408.
(22) Shimamori, H.; Okuda, T. *J. Phys. Chem.* **1994**, *98*, 2576.
(23) Xiang, B.; Kevan, L. *Langmuir* **1995**, *11*, 860.
(24) Nakai, H.; Konno, M.; Kosuge, S.; Sakuyama, S.; Toda, M.; Arai, Y.; Katube, N.; Miyamoto,T.; Okegawa, T.; Kawasaki, A. *J. Med. Chem.* **1988**, *31*, 84.
(25) Hiromitsu, I.; Kevan, L. *J. Phys. Chem.* **1989**, *93*, 3218.
(26) Herson, W. D.; Hager, L. P. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. Vll.
(27) Kevan, L. In *Time Domain Electron Spin Resonance*; Kevan, L., Schwartz, R. N., Eds.; Wiley: New York, 1979; Chapter 8.
(28) Yoon, K. B. *Chem. Rev.* **1993**, *93*, 321.